

15.8200
15.8530

81

40906

8/191/62/000/010/001/010
B101/B106

3

AUTHORS:

Heyman, M. B., Kovarskaya, B. M., Levantovskaya, I. I., Dral-
yuk, G. V., Yazvukova, M. P., Sidorov, V. A., Kochetkov, V. M.
Trosman, G. M., Tatevos'yan, G. O., Kusanetsova, I. B.

TITLE:

Stabilization of polyamide films for agriculture

PERIODICAL:

Plasticheskiye massy, no. 10, 1962, 6 - 8

TEXT: Protection of polyamide films, type 54, as used in hothouses and
silos, from effects of photo- and thermooxidation was tested by trying
various additives under various test conditions. The following were added
as ultraviolet light absorbers: 2-hydroxy-4-methoxy-benzophenone OMBP
(OMBP) (I), 2-hydroxy-4-alkoxy-benzophenone (a mixture of benzophenones
with various alkoxy groups of the type OC_7H_{15} , OC_8H_{17} , or OC_9H_{19}) (II), and
2-hydroxy-5'-methyl-benzotriazole (Winuvin) (III). As antioxidants, KI
and copper naphthenate and organic stabilizers of the following type were
used: 1) derivatives of aromatic amines; 2) phenol derivatives; 3) aromatic
oxamines; 4) 2,6-ditert-butyl-4-methyl-phenyl-pyrocatechin phosphite (Ionoll).

Card 1/2

6

5
S/191/62/030/010/001/010
B101/B106

Stabilization of ...

Polymide film blanks produced by condensation, namely hexamethylene adipate and ϵ -caprolactam at 260°C in an N-atmosphere, were subjected to thermo- and photooxidative action. Light sources were carbon-arc and mercury-quartz lamps, type ПРК-2 (PRK-2). Temperature in the test chamber was $70 \pm 2^\circ\text{C}$. Thermooxidation measured by the drop in oxygen pressure was eliminated most efficiently by the pyrocatechin esters and phenyl- β -naphthyl-amine. It was found that stabilizers of the OMBF and Tuvin types act as antioxidants. Photooxidation experiments showed the following results: in most cases the elongation at rupture dropped even on initial exposure. After 200 hrs of exposure time, breaking tenacity of both stabilized and nonstabilized films fell by approximately 20 - 25%. Ageing time until embrittlement was determined. Without an inhibitor it began after 190 hrs of exposure to the light of an arc lamp. Optimum results were obtained with pyrocatechin esters (250 hrs), KI + copper naphthenate (260 hrs) and (Santovar) O ((2,6-di-tert-butyl-hydroquinone)) (240 hrs). Different action of the light from the arc lamps and the mercury lamps was explained by spectrum differences. Further field tests are recommended. There are 3 figures and 1 table.

Card 2/2

TATEVOS'YAN, G.O.

At the Exhibition of Achievements of the National Economy
of the U.S.S.R.. Glass reinforced plastics as building
materials. Plast.massy no.10:71-73 '62. (MIRA 15:11)
(Glass reinforced plastics—Exhibitions)

TATEVOS'YAN, G.O.

Exhibition of the equipment and industrial products of
Italian firms. Plast.massy no.10:73-74 '62. (MIRA 15:11)
(Italy--Plastics industry--Equipment and supplies)
(Moscow--Exhibitions)

L1918

S/191/62/000/011/014/019
B101/B186

68330

AUTHORS: Tatevos'yan, G. O., Losev, I. P., Kuznetsova, I. B.

TITLE: Chemical analysis of polyvinyl chloride plastics subjected to photoaging

PERIODICAL: Plasticheskiye massy, no. 11, 1962, 59-62

TEXT: Polyvinyl chloride plastics of the types 230, 239, 251, and 489 with a composition of 56-70% polyvinyl chloride, 21-33% liquid plasticizer, and about 10% stabilizer were irradiated at 70°C by carbon arc lamps (680-1000 hrs) or mercury vapor lamps (24-180 hrs). The changes in composition, tensile strength, and resistivity were studied. The composition was arrived at successive extractions with ether, acetone, benzene, and chloro benzene, by determining how much plasticizer remained in the plastic after irradiation, and by determining the chlorine content. Results: (1) The loss of plasticizer as referred to the total weight of plastic was 6-10% after irradiation by arc lamps, and 11-15% after irradiation by Hg vapor lamps. It is noted that determination of the weight loss alone leads to deviating data. (2) The chlorine content decreased, but on irradiating with Hg lamp this was masked by the intense loss of

Card 1/2

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Chemical analysis of polyvinyl ...

S/191/62/000/011/014/019
B101/B186

plasticizer. (3) The resistivity of non-irradiated specimens was in the order of 10^{12} ohm-cm, that of specimens irradiated by arc lamps in the order of 10^{13} , and that of specimens irradiated with Hg light was 10^{14} ohm-cm. (4) The tensile strength of non-irradiated specimens was 217-280 kg/cm². Under arc lamp irradiation it dropped to 105-176 kg/cm²; under Hg light irradiation, it dropped at first, but then increased to 238-328 kg/cm². Conclusions: Destruction processes prevail in arc lamp irradiation, and structuration processes in Hg light irradiation. Structuration processes increase the tensile strength and the resistivity, and accelerate the volatilization of the plasticizer since structurized PVC is no longer soluble in it. There are 5 tables.

Card 2/2

TATEVOS'YAN, G. G.

Exhibition of Achievements of the National Economy of the
U.S.S.R. Plast. massy no.11:75 '62. (MIRA 16:1)

(Plastics—Exhibitions)

TATEVOS'YAN, G.O.

Exhibition of Achievements of the National Economy of the
U.S.S.R.; scientific research work of institutions of higher
learning. Plast. massy no.12:1-2 '62. (MIRA 16:1)
(Scientific apparatus and instruments—Exhibitions)

S/191/63/000/002/013/019
B101/B186

AUTHORS: Tatevos'yan, G. O., Kuznetsova, I. B.
TITLE: Long-time and alternating effects of water and moist air on plastics
PERIODICAL: Plasticheskiye massy, no. 2, 1963, 52-58

TEXT: With a view to uses of plastics in building and agriculture the following materials were tested for changes in physicomachanical and dielectric properties due to the effect of water and moisture: press-molded homogeneous thermoplastics such as styrene copolymers CHT (SNP), MC (MS), and MCH (MSN), polystyrene, polypropylene, polyamide 68, Butvar, ethyl cellulose etrol; molded powder-filled inhomogeneous thermosetting plastics based on phenol formaldehyde resins including such modified with rubber, PVC, or polyamide resin; monolithic phenol aldehyde plastics based on novolac resins with organic curing agent; thermosetting laminated plastics based on phenol furfural or polyester resins with glass fiber reinforcement. The tests covered the water adsorption at 20 or 40°C and the adsorption of moisture at 40°C during 1-56 days by weighing the moistened and dried

Card 1/2

Long-time and alternating ...

S/191/63/000/002/013/019
B101/B186

specimens. The change in weight after five 24-hr. dippings into 20°C water and drying at 40°C was determined. Conclusions drawn from the tabulated data: (1) Permanent action of water or moisture produces the greatest changes of physicomachanical and dielectric properties in thermosetting plastics, and the least in thermoplastics. The great changes in thermosetting plastics are due to capillary formations. (2) Among thermosetting plastics the highest water adsorption is reached by materials based on novolac phenol formaldehyde resins, the lowest by materials based on resol or novolac and resol resins modified by thermoplastics. (3) 20°C water changes the properties in the same way as 40°C air moisture, so the simpler 20°C water test is to be preferred. (4) Long-time action of water changes the properties more than alternate moistening and drying. (5) The tests can be used to estimate the utility of plastics under atmospheric influences and to help in their proper selection. There are 3 tables.

Card 2/2

S/191/63/000/003/016/022
B101/B186

AUTHORS:

Kuznetsova, I. B., Tatevos'yan, G. O.

TITLE:

Standard method for testing the weather- and lightproofness of plastics

PERIODICAL: Plasticheskiye massy, no. 3, 1963, 54-59

TEXT: In 1963, the ГОСТ no. 10226-62 (GOST no. 10226-62) standard published in Standartizatsiya, no. 3, 1962, was introduced in the USSR to standardize the testing of weatherproofness and lightproofness plastics. Some explanations and recommendations for applying this standard are given. Weatherproofness is tested in various climatic regions. The specimens are mounted on frames fixed at an angle of 45° facing the south. Two of these frame constructions are described. Equipment such as heliograph, Yanishevskiy pyranometer, ombrometer, thermometer, psychrometer, and anemometer is recommended for special meteorological stations in cases where no regular reports are obtainable from a state meteorological station. Calibration of the pyranometer according to the actinometer data from a State meteorological station is briefly described. The laboratory conditions, the

Card 1/2

APPROVED FOR RELEASE: 07/16/2001

Standard method for testing ...

S/191/63/000/003/016/022
B101/B186

АНПСТ-2-4-2 (AIPST-2-4-2) apparatus is used. It consists of a case mounted on a rotating holder, for testing the samples in horizontal or vertical position, two carbon-arc lamps, four mercury-vapor lamps, two fans to maintain a temperature of 20-90°C, a moistening apparatus, and signaling system which indicates irregularities or when the rotating cases stop or a lamp fails, etc. Measurement of the light intensity with the Yanishevskiy pyranometer is described. There are 3 figures and 3 tables.

Card 2/2

TATEVOS'YAN, G.O.

Exhibition of Achievements of the National Economy of the
U.S.S.R. Plastic materials used in machinery manufacture.
Plast. massy no.3:75-76 '63. (MIRA 16:4)

(Machinery industry--Equipment and supplies)
(Plastics--Exhibitions)

TATEVOS'YAN, G.O.

Exhibition of Achievements of the National Economy of the
U.S.S.R.; articles made of thermoplastics manufactured by
centrifugal casting. Plast.massy no.5:77-78 '63.

(MIRA 16:6)

(Plastics—Exhibitions)

TATEVOSYAN, G.O.

Exhibition of Achievements of the National Economy of the U.S.S.R.
Plast.massy no.7:75-77 '63. (MIRA 16:8)
(Plastics--Exhibitions)

TATEVOS'YAN, G.O.; KUZNETSOVA, I.B.; LAMINA, R.A.

Aging of polystyrene under the effect of ultraviolet light.

Plast. massy no.8:66-67 '63.

(MIRA 16:8)

(Styrene polymers)

(Ultraviolet rays)

L 18953-63
RM/WW/MAY

EPR/EWP(j)/EPF(c)/EWT(m)/BDS AFFTC/ASD Ps-4/Po-4/Pr-4

ACCESSION NR: AP3006531

S/0191/63/000/009/0010/0012

AUTHORS: Tatevos'yan, G. O.; Losev, I. P. (Deceased); 13
Kuznetsova, I. B.

TITLE: The effect of plasticizer¹⁵ upon light aging of vinyl blend.

SOURCE: Plasticheskiye massy*, no. 9, 1963, 10-12.

TOPIC TAGS: polyvinylchloride, vinyl blend, light aging, plastics, plasticizer.

ABSTRACT: Authors showed that the aging¹⁵ process of a plasticizer does not increase its specific gravity, but increases its acidity, which indicates a decrease of the specific volume of electrical resistance. The resistance of polyvinylchloride plasticizer to the effects of light energy is primarily determined by aging which takes place in the polyvinylchloride resin.¹⁵ As a result of this aging, the mutual solubility in the resin and plasticizer changes.

Card 1/2

L 18953-63

ACCESSION NR: AP3006531

The observed continuous change of plasticizer quantity in the aging process of vinyl blend by light did not show a decisive effect upon the stability. Orig. art. has: 3 tables.

ASSOCIATION: none.

SUBMITTED: 00

DATE ACQ: 30Sep63

ENCL: 00

SUB CODE: CH

NO REF SOV: 002

OTHER: 001

Card 2/2

L 16198-63 EPR/EWP(j)/EPP(c)/EPP(n)-2/EWT(1)/EWG(k)/EWT(r)/EES/t-2/
 EEC(b)-2/ES(s)-2--AEDC/AFFTC/ASD/ESD-3/SSD--Ps-4/Pc-4/Pr-4/Pu-4/Pz-4/Pt-4/Pq-4--
 RM/AT/WH/WW/MAY
 ACCESSION NR: AP3006545 S/0191/63/000/009/0066/0067

AUTHOR: Tatevos'yan, G. O. 117
 100

TITLE: Exposition of the achievements of the national economy of
 the USSR. Scientific research at the exposition

SOURCE: Plasticheskiy massy*, no. 9, 1963, 66-67

TOPIC TAGS: Vinol PK, blood anticoagulant, blood substitute, macro-
 molecular blood anticoagulant, macromolecular blood substitute, 4-
 hydroxycoumarin, pelentan, parenteral administration, oxidation
 resistance, intravenous administration, noncoagulation, pro-
 thrombin effect, graft copolymerization, surface graft copolymeriza-
 tion, organic polymeric semiconductor, organic semiconductor, synthe-
 sis, polymeric Schiff base, polyphenylene, polyazine, polyaminoqui-
 none, polynitrile, polymeric chelate compound, conjugated bond,
 thermoelectric power, electrical conductivity, oxidation resistant
 coating, coating, steel coating, cast iron coating, air oxidation
 protection, carbon coating, graphite coating, silicon treatment.

Card 1/4

L 16198-63
ACCESSION NR: AP3006545

4

silicate glass, molybdenum disilicide, silicon carbide, aluminum oxide sublayer, heat resistance, oxidation resistance

ABSTRACT: Exhibits showing the results of research conducted at the Institutes of the Academy of Sciences SSSR have been placed on display. 1) Vinol PK, a macromolecular blood anticoagulant and blood substitute, has been developed at the Institut vy*sokomolekulyarny*kh soyedineniy (Institute of Macromolecular Compounds). It is 1/2—1/3 as toxic as low-molecular anticoagulants, which are derivatives of 4-hydroxycoumarin. Its action lasts 4—5 times as long as that of low-molecular pelentan. It is equally effective in parenteral and intravenous administration. It sharply forestalls coagulation and increases the prothrombin index. 2) Graft copolymers have been produced by a new method developed at the Institut elementoorganicheskikh soyedineniy (Institute of Organoelemental Compounds). Polymers are grafted onto the surface of fabricated plastic articles. Copolymerization is activated by brief treatment in hot air. Grafting modifies the surface properties but leaves the bulk of the article.

Card 2/4

L 16198-63

ACCESSION NR: AP3006545

unchanged. 3) The Institut neftekhimicheskogo sinteza (Institute of Petrochemical Synthesis), Institut khimicheskoy fiziki (Institute of Chemical Physics), Institut poluprovodnikov (Institute of Semiconductors), and Institut elektrokhimii (Institute of Electrochemistry) have synthesized and studied the properties of organic polymeric semiconductors, some of which are selective and highly effective catalysts. The semiconductors were prepared either by direct synthesis (e.g., polymeric Schiff bases, polyphenylenes, polyazines, polyaminoquinones, polyatrilles, polymeric chelates) or by controlled chemical changes in the backbones of polymers to form a system of conjugated bonds. The thermoelectric power of most of the semiconducting polymers varies between 30 and 500 microvolts per degree. Polymers can be prepared with a predetermined electrical conductivity in the 10^{-12} — 10^{-2} ohm-cm range. Production of semiconducting polymer fibers, fabrics, and films will make possible their use in semiconductor devices. 4) Oxidation-resistant coatings have been developed at the Institut khimii silikatov (Institute of Silicate Chemistry). Glass, metal carbide, metal borosilicide, and mixed coatings for steel

Card 3/4

L 16198-63
ACCESSION NR: AP3006545

2

and cast iron have been developed. Coatings up to 0.2 mm thick adhere firmly to the metal and protect it against oxidation in air at 900C for several hundred hours. These coatings withstand thermal shock of several 20—900—20C cycles. Coatings for carbon and graphite materials have also been developed. Pure silicon-treated carbon or graphite were coated with a mixture of refractory silicate glass, molybdenum disilicide, and silicon carbide in various ratios. The coatings protected carbon and graphite for 100 hr at 1200C. When applied on Al_2O_3 sublayers, the coatings protected the materials for 100 hr at 1400C and for a short time at 1800C. The coatings withstood 100 20—1400—20C thermal cycles.

ASSOCIATION: none

SUBMITTED: 00

DATE ACQ: 30Sep63

ENCL: 00

SUB CODE: MA

NO REF SOV: 000

OTHER: 000

Card 4/4

TATEVOS'YAN, G.O.

Exhibition of Achievements of the National Economy of the U.S.S.R.;
new devices for the investigation of macromolecular compounds.
Plast,massy no.10:69-71 '63. (MIRA 16:10)

TATEVOSYAN, G.O.

Exhibition of Achievements of the National Economy of the
U.S.S.R. Plast. massy no.11:73-74 '63. (MIRA 16:12)

TATEVOS'YAN, G.O.

Japanese exhibition of machinery and instruments. Plast.massy no.12:
65-68 '63. (MIRA 17:2)

TATEVOS'YAN, G.O.

Equipment for the plastics industry at the Austrian Exhibition of Specialized Tools and Machinery. Plast.massy no.3:
70-73 '64. (MIRA 17:3)

TATEVOS'YAN, G.O.

Polyamides at the Exhibition of Achievements of the National Economy
of the U.S.S.R. Plast.massy no.7:67-69 '64. (MIRA 17:10)

TATEVOSYAN, G.O.

New instruments at the Exhibition of Achievements of the National
Economy of the U.S.S.R. Plast. massy no.8:73 '64.

(MIRA 17:12)

ACCESSION NR: AP4045022

S/0191/64/000/009/0032/0037

AUTHOR: Kuznetsova, I. B., Tatevos'yan, G. O.

TITLE: Change in the properties of polyamide film under the influence of light

SOURCE: *Plasticheskiye massy**, no. 9, 1964, 32-37

TOPIC TAGS: polyamide, light, aging, spectroscopy, tensile strength, elongation, light absorption, polyamide film, film PK-4

ABSTRACT: The changes in the properties of polyamide film PK-4 during aging under atmospheric and laboratory conditions were studied by spectroscopy under the separate or combined influence of artificial changes in climate. A colorless unstabilized PK-4 film was used as the test sample, with an elongation at break $\epsilon_0 = 292\%$ and maximum tensile strength $\sigma_0 = 388 \text{ kgs/cm}^2$. The test sample was subjected to atmospheric aging on a laboratory apparatus, to atmospheric aging in suspension, excluding direct solar radiation, to artificial aging at 70C under artificial light (500W incandescent lamp, arc and mercury lamps), and finally to aging under the influence of moisture with arc and mercury lamps. The following characteristics were determined: yellowing factor, % maximum tensile strength (σ); relative elongation at break (ϵ , %) for 80-mm-long and

Card 1/3

ACCESSION NR: AP4045022

8-mm-wide strips; the monomer content, by extraction with boiling water for 15 hours; the molecular weight, from the viscosity of a 0.1% solution in 40% H_2SO_4 at room temperature; and the ultraviolet and infrared absorption spectra. The experimental data are plotted. ξ -t and ζ -t curves show that variations in relative humidity and atmospheric drying greatly affect the properties. The process of thermal aging proceeds relatively slowly, however. At a temperature of 45-46C in visible light, the change in properties can be attributed to light aging. Yellowing of the film appeared after 145 and 75 hours of irradiation at intensities of 0.442 and 0.866 cal/cm² min., respectively. The mol. weight dropped from 23,500 to 19330-19062. Visible light together with atmospheric oxygen affect the polyamide film markedly causing its destruction. In samples kept in distilled water until the weight changed, ξ increased to 365%, and ζ decreased to 267 kgs/cm²; in dried samples the opposite occurred. In addition to moisture, the monomer content also affects the film properties. The effect of heat under light from incandescent and mercury-quartz lamps was also studied. The combined effect of heat, moisture and light was investigated, and analytical data for monomer content and oxygen content are tabulated. The absorption of light by the film before and after aging under different conditions was investigated and the changes in light transmission in the ultraviolet and infrared regions of the spectrum during aging are discussed in detail. Under the influence

2/3

Card

ACCESSION NR: AP4045022

of heat and visible light, the absorption in the region 250-290 $m\mu$ increased rapidly; later it increased less rapidly in the range 290-680 $m\mu$. During aging under atmospheric conditions, the general light absorption decreased in all regions of the spectrum. It is important that the light absorption is smaller after aging in all cases, especially marked changes being found in the regions 800-900, 1800-2800, and 3600-4000 cm^{-1} . Orig. art. has: 6 figures and 2 tables.

ASSOCIATION: None

SUBMITTED: 00

ENCL: 00

SUB CODE: MT *PP*

NO REF SOV: 021

OTHER: 015

Card 3/3

FRENKEL', M.D.; DVORKINA, T.V.; TATEVOS'YAN, G.O.

Methods for the determination of the brittleness temperature
for plastics. Standartizatsia 28 no.1:45-53 Ja '64.

(MIRA 17:1)

TATEVOS'YAN, G.O.

Exhibition of Achievements of the National Economy of the U.S.S.R.
Plast.massy no.6:71-72 '64. (MIRA 18:4)

TATEVOS'YAN, G.O.

New polymers at the Exhibition of Achievements of the National
Economy of the U.S.S.R. Plast. massy no.12:63 '64.

(MIRA 18:3)

--- 20 --- EWP(A)/EWP(M)/EWP(V)/EPP(C)/EWO(V)/EWP(C)/EWP(V)/EWP(J)/T/EWP(K)/

AUTHOR: Nikol'skoy, A.M. Kuznetsova, L.M. Tarevna Jan, L.M.

--- 1 --- problem of following the aging of plastic by non-destructive mechanical tests 16

SOURCE: Plasticheskiye massy, no. 1, 1965, 52-57

TOPIC TAGS: polymer aging, polymer mechanical property, hardness measurement, 201

Card 1

ASSOCIATION: none

SUBMITTED: 00

ENCL: 02

SUB CODE: MT

TATEVOS'YAN, G.O.
TATEVOS'YAN, G.O.

New exposure at the Exhibition of Achievements of the National
Economy of the U.S.S.R. Plast. massy no. 6172-72 '68.

(MIRA 18:8)

USSR/Soil Science - Genesis and Geography of Soils.

J

Abs Jour : Ref Zhur Biol., No 22, 1958, 99993

Author : Tatevosyan, G.S.

Inst : Armenian Scientific-Research Institute of Agriculture

Title : The Mountain-Meadow Peat Soils of Shamshalinskiy Rayon

Orig Pub : Byul. nauchno-tekhn. inform. Arm n.-1. in-t zemledeliya,
1957, No 3, 13-16

Abstract : No abstract.

Card 1/1

- 21 -

COUNTRY : USSR
 CATEGORY : Soil Science. Soil Genesis and Geography. J
 ABS. JOUR. : RzhBiol., No. 3 1959, No. 10654
 AUTHOR : Tatevosyan, G. S.
 INST. : Academy of Sciences, Armenian SSR
 TITLE : On the Change of Mountain-Forest Brown Soils of
 Shemshadinskiy Rayon, Armenian SSR to Steppe Soils.
 ORIG. PUB. : Aykakan SSR Gitutyunneri Akademiye. Tegekegir.
 ABSTRACT : Biologitskan yev gyukatntesakan gitutyunner, Izv. AN *)
 The territory surveyed is situated on the northwestern
 spur of Murguzskiy Ridge within the altitude range of
 1500-1600 meters above sea level. The chief cause of the
 change in this rayon of forest vegetation by steppe forma-
 tions is man's agricultural activity. Under the influ-
 ence of mountain-steppe vegetation, the mountain-forest
 brown soils gradually acquire a black color, the forest
 *)ArmSSR. Biol. i s.-kh. n., 1958, 11, No. 4, 75-86

CARD: 1/3

8

COUNTRY :
 CATEGORY :
 ABS. JOUR. : RZhBiol., No. 1952, No. 10624
 AUTHOR :
 INST. :
 TITLE :
 ORIG. PUB. :
 ABSTRACT : litter is replaced by turf horizon. The nut-like structure changed to a nut-like, powdery-granular structure, accumulation of humus, and an increase in the content of alkali earth bases takes place. The absorbed H is replaced by alkali earth metals, the mildly acid reaction of the soil becomes neutral. The mountain-forest brown soils, changed to steppes, approach the so-called after-forest chernozems in morphological and physico-chemical properties. The mountain-forest brown soils changed slightly to steppe also stand out as a group of transitional soils between the mountain-forest brown soils and

END: 2/3

COUNTRY :
CATEGORY :

ASS. SOUR. : RZhSiel., No. 1959, No. 10654

AUTHOR :
INST. :
TITLE :

ORIG. PUB. :

ABSTRACT : after-forest chernozems. The general adoption of
xerophytes on the territory of Armenia in recent decades
contributes to the processes of transformation to steppes
in the rayon described. -- P. V. Shramko

REF: 2/3

TATEVOSYAN, G. S.: Master Biol Sci (diss) -- "The soils of Shamshadinskiy Rayon, Armenian SSR". Kishinev, 1959. 16 pp (Min Higher Educ USSR, Kishinev State U), 150 copies (KL, No 16, 1959, 107)

10

ca

Processes and Properties Index

Catalytic hydrogenation of diphenylfulvene. B. A. Kazanskii and G. T. Tatevosyan. *J. Gen. Chem.* (U. S. S. R.) 8, 1428-37 (1938).—The hydrogenation of diphenylfulvene (I) was repeated in the presence of Pt and Pd black in alc., AcOH, Et₂O and cyclohexanone in the cold (cf. C. A. 30, 4824). Contrary to previous findings, the addn. of the 1st mol. H proceeds slowly with only gradual and incomplete disappearance of the fulvene red color. The catalyzed is a complex mixt., contg. chiefly unaltered I. The presence of the dihydro deriv. was not detd. I absorbs 2 mols. H quite readily, giving *diphenylmethanocyclopentadiene*, b.p. 180-1°, m. 62-2.5°. It is oxidized with HNO₃ to Ph₂CO. The addn. of the 3rd mol. H proceeds very slowly to give *cyclopentylidiphenylmethane* previously described. The successive satn. of the 2 double bonds proceeds more distinctly with Pd in alc. Its rate and the compn. of the catalyzates vary with the solvents and catalysts used in the reaction. C. B.

ASM-SEA METALLURGICAL LITERATURE CLASSIFICATION

FROM	TO	DATE	CLASSIFICATION
1	2	3	4
5	6	7	8
9	10	11	12
13	14	15	16
17	18	19	20
21	22	23	24
25	26	27	28
29	30	31	32
33	34	35	36
37	38	39	40
41	42	43	44
45	46	47	48
49	50	51	52
53	54	55	56
57	58	59	60
61	62	63	64
65	66	67	68
69	70	71	72
73	74	75	76
77	78	79	80
81	82	83	84
85	86	87	88
89	90	91	92
93	94	95	96
97	98	99	100

COMMON ELEMENTS		PROCESSES AND PROPERTIES INDEX	
1	2	3	4
5	6	7	8
9	10	11	12
13	14	15	16
17	18	19	20
21	22	23	24
25	26	27	28
29	30	31	32
33	34	35	36
37	38	39	40
41	42	43	44
45	46	47	48
49	50	51	52
53	54	55	56
57	58	59	60
61	62	63	64
65	66	67	68
69	70	71	72
73	74	75	76
77	78	79	80
81	82	83	84
85	86	87	88
89	90	91	92
93	94	95	96
97	98	99	100

CA

Influence of the substituents on the velocity of catalytic hydrogenation of certain trisubstituted ethylenes in the presence of platinum. B. A. Karanskil and G. T. Tatarskiy. *Gen. Chem. (U. S. S. R.)* 9, 1464-64 (1934).

1-Methyl-2,2-diethyl- (I), 1,2-dimethyl-1-phenyl- (II), 1,1-dimethyl-2,2-diphenyl- (III) and triphenylethylene (IV) were prepared by known methods. The individual ethylenes and equimol. mixts. of I with II, III and IV were hydrogenated in 96% alc. in the presence of Pt black at room temp. by the method described in an earlier paper (C. A. 33, 42014). The graphic results show that the velocity of hydrogenation of trisubstituted ethylenes decreases with increasing no. of aryl substituents in the mol. The drop in velocity is particularly sharp with the introduction of a 2nd aryl substituent. The hydrogenation of mixed hydrocarbons proceeds simultaneously. However, because of the different character of substituents and the resulting difference in the hydrogenation velocity of the individual hydrocarbons and the distribution of H between the components of mixts., the reaction shows some selectivity, which becomes more pronounced with greater no. of Ph substituents in the 2nd component.

Inst. Org. Chem., ASUSSR

Chas. Blanc

ASS-314 METALLURGICAL LITERATURE CLASSIFICATION

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PROCESSES AND PROPERTIES INDEX																																																																																																							
<p>Influence of the substituents on the velocity of catalytic hydrogenation of certain trisubstituted ethylenes in the presence of palladium black. H. A. Kazanskii and G. I. Talyrova, <i>J. Gen. Chem.</i> (U. S. S. R.) 9, 2206-02 (1939).--The hydrogenation of 1-methyl-2,2-diethyl- (I), 1,1-dimethyl-2-phenyl- (II), 1-methyl-2,2-diphenyl- (III) and triphenylethylene (IV) and equimol. mixts. of I with II, III and IV was repeated in the presence of Pd black instead of Pt black as previously used (C. A. 34, 2780). The velocity of hydrogenation of trisubstituted ethylenes with Pd increases sharply with substitution of 1 and 2 Ph for aliphatic radicals in contrast to the reaction with Pt, and considerably increases with 3 Ph substituents. Hydrogenation of binary mixts. proceeds selectively with a considerably greater rate of addn. of the 1st H mol. to the aromatic components (87-96%) than to I (4-13%). Comparative tests in the hydrogenation of I with and without the addn. of iso-BuPh, Ph₃CHEt and Ph₃CH-CH₂Ph showed conclusively that the retardation of I hydrogenation is caused by poisoning of the catalyst by the aromatic hydrocarbons formed in the reaction. The rate of retardation increases with increasing no. of aryl substituents in the mol. This effect was further confirmed by the retardation of hydrogenation of 4-nonen in the presence of C₆H₆.</p> <p style="text-align: right;">Chas. Blanc</p>																																																																																																							
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PROCESSES AND PROPERTIES INDEX

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Gaseous products of the action of zinc dust on 2,4-dichloro-2-butene. G. T. Tatevnyan and A. A. Varianyan (Chem. Inst. Armenian Acad. Sci. S.S.R.). *Dokl. Akad. Nauk Arm. SSR*, 1961, No. 8, 76-8 (in Russian).—2,4-Dichloro-2-butene (25 g.) in 50 cc. 80% EtOH was treated with 30 g. Zn dust with cooling and collection of gases; the mist. was finally heated to 80-90°. The products were identified as 2-butene and 1,3-butadiene by means of their bromides. G. M. K.

ASS-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND COLUMNS										3RD AND 4TH COLUMNS									
PROCESSES AND PROPERTIES INDEX																			
<p>Dehydration of methylcyclobutylcarbinol. G. J. Tait, V. A. Terzyan and A. G. Terzyan (Chem. Inst. Armenian Acad. Sci. U.S.S.R.). <i>Bull. Armenian Branch Acad. Sci. U.S.S.R.</i>, No. 1/2, 73-8 (in Russian).—Methylcyclobutylcarbinol (12.7 g.) was heated with 80 g. conc. (CO_2H), with slow distn. to yield 43.3% 1-methylcyclopentene, b_p 70-1°, d_4^{20} 0.7811, n_D^{20} 1.4344, which was identified by KMnO_4 oxidation. G. M. Komolodt</p>																			
<p>ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION</p>																			
FROM SYMBOLS										FROM POWERS									
<p>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20</p>										<p>21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40</p>									

117 AND 120 DRUMS

PROCESSES AND PROPERTIES INDEX

101 AND 104 CRUMBS

ca

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Action of hydrobromic acid on methylcyclobutylcarbinol.
G. T. Tatevanyan and M. I. Melikyan (Chem. Inst.
Armenian Acad. Sci. U.S.S.R.). *Bull. Armenian Branch
Acad. Sci. U.S.S.R.* 1944, No. 5/6, 23-6 (in Russian with
English summary).—Methylcyclobutylcarbinol, b. 138-
0°, d₄²⁰ 0.8974, n_D²⁰ 1.4448, (7 g.) was treated at 0° with HBr
cc. 111 cc. (d. 1.8); after standing for 1 day the mixt. was
gently boiled for 25-30 min. to yield 7.02 g. 1-methyl-1-
bromocyclopentane (I), b. 74-0°, d₄²⁰ 1.3004, n_D²⁰ 1.4821.
I when heated with quinoline to 190-200° gave 79% 1-
methylcyclopentene, b. 69-71°, d₄²⁰ 0.7812, n_D²⁰ 1.4331,
which was identified by oxidation with KMnO₄.
G. M. Kozolotoff

ASB-11A METALLURGICAL LITERATURE CLASSIFICATION

117 AND 120 DRUMS

101 AND 104 CRUMBS

1ST AND 2ND ORDERS																											3RD AND 4TH ORDERS																														
PROCESSES AND PROPERTIES INDEX																																																									
<div style="font-size: 2em; margin-bottom: 10px;">CA</div> <div style="writing-mode: vertical-rl; transform: rotate(180deg); position: absolute; left: -40px; top: 50%;">COUNCIL ELEMENTS</div> <div style="writing-mode: vertical-rl; transform: rotate(180deg); position: absolute; right: -40px; top: 50%;">COUNCIL ELEMENTS</div>					<p><i>Bis(3-chlorocrotyl)barbituric acid.</i> G. T. Tatevnyan and M. G. Tuteryan (Chem. Inst. Armenian Acad. Sci. S.S.R.). <i>Bull. Armenian Branch Acad. Sci. U.S.S.R.</i> 1944, No. 5/6, 29-35 (in Russian with English summary).—To 6.3 g. Na in 71 g. abs. EtOH there was added 44 g. CH₃(CO₂Et), and the solidified mixt. was treated with 35 g. 2,4-dichloro-2-butene with cooling and stirring. After heating on a steam bath for 4 hrs., the mixt. was cooled and treated with NaOEt (from 6.3 g. Na and 71 g. EtOH), followed by 35 g. of 2,4-dichloro-2-butene. The mixt. was again heated for 4-5 hrs. to yield, after distn. of EtOH and treatment with acidified water, <i>di-Et bis(3-chlorocrotyl)malonate</i>, b.p. 101-3°, h_p 168-70°, h_f 172-4°, d₄²⁰ 1.1437, n_D²⁰ 1.4961. Urea (6 g.) in 55 cc. abs. EtOH was treated with 31.7 g. of the above ester, then added to 5 g. Na in 55 cc. abs. EtOH, and the mixt. heated for 3 hrs. at 70-80°, followed by refluxing for 3 hrs. On cooling, 2.5 g. urea was added and the mixt. was boiled for 6 hrs.; the EtOH was distilled off, and the residue was treated with 50 cc. water and 20 cc. HCl (d. 1.165); after standing overnight the <i>bis-(3-chlorocrotyl)barbituric acid</i> was filtered off; m. 160-70° (from EtOH), 62%. Hydrolysis of either the barbituric acid or the malonic ester by NaOH gave <i>bis(3-chlorocrotyl)malonic acid</i>, m. 130-1° (from water). By heating of the latter over a free flame, followed by distn. in vacuo, 87.3°; <i>bis(3-chlorocrotyl)acetic acid</i>, b_p 183-5°, n. 37.8° was obtained. The <i>bis(chlorocrotyl)barbituric acid</i> is very toxic and has no soporific effect. G. M. K.</p>																																																				
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COMMON ELEMENTS		COMMON VARIANTS INDEX	
137 AND 138 CODES		140 AND 141 CODES	
ca		10	
<p>Acid saponification of 5-chloro-4-hexenoic acid. (G. T. Tatevosyan, M. I. Melikyan, and M. G. Tuteryan (Chem. Inst. Armenian Acad. Sci. S.S.R.). <i>Bull. Armenian Branch Acad. Sci. U.S.S.R.</i> 1964, No. 5/6, 37-44 (in Russian with English summary).—To ethyl malonic ester (from 8.5 g. Na and 50.5 g. $\text{CH}_3(\text{COO})_2\text{C}_2\text{H}_5$) in 90 g. abs. EtOH there was added dropwise with cooling 47.5 g. 2,4-dichloro-3-butene, after which the mixt. was refluxed for 3 hrs. and was allowed to stand overnight to yield, after distn. of the EtOH and acidification with dil. H_2SO_4, 41.87% <i>dl-Et (3-chlorocrotyl)malonate</i>, b_p 121.5-2.5°, d_4^{20} 1.1089, n_D^{20} 1.4880. To 80 g. KOH in 40 g. H_2O there was added 44.87 g. of the above ester and the mixt. was carefully heated until reaction set in. After boiling for 15 min. the mixt. was cooled, acidified with HCl, and extd. with Et_2O. Removal of Et_2O gave (3-chlorocrotyl)malonic acid (50.5%), m. 94-6°. Heating of this over a free flame, followed by distn. <i>in vacuo</i>, gave 94.96% 5-chloro-6-hexenoic acid, b_p 128-8.5°, d_4^{20} 1.1434, n_D^{20} 1.4738. Treatment of the latter with concd. H_2SO_4 with cooling gave, after standing for 1 day, 61.2% γ-acetylbutyric acid hydrate, m. 37-8°; semicarbazone, m. 168-9°.</p> <p>G. M. Kozulapov</p>			
ASAC-51A METALLURGICAL LITERATURE CLASSIFICATION			
FROM DIVISION		FROM DIVISION	
137 AND 138 CODES		140 AND 141 CODES	

1ST AND 2ND DEGREE										3RD AND 4TH DEGREE									
PROCESSES AND PROPERTIES INDEX																			
<p>10</p> <p>Acid hydrolysis of 2-chloro-2-hepten-6-one. ¹⁰ T. Tatevossyan, M. I. Melikyan, and M. G. Tutervan <i>J. Chem. Acad. Sci. Armenian S.S.R., Brevan</i>. <i>Proc. Acad. Sci. Armenian S.S.R.</i> 1945, II, No. 1, 9-13 (in Russian with English summary). — 2-Chloro-2-hepten-6-one (12 g.) was treated with cooling with 20 cc. 84.5% H₂SO₄; after standing for 2 days the mixt. was diltd. and neutralized. After extrn. with Et₂O, the ext. was dbd. to yield 70.30% 1-methyl-1-cyclohexen-7-one, bp 61-4°, n_D²⁰ 1.4816, d₄²⁰ 0.9758; semicarbazone, m. 181-8° (from EtOH).</p> <p>G. M. Kowalskoff</p>										<p>10</p>									
<p>ACID-ALK METALLURGICAL LITERATURE CLASSIFICATION</p>																			
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1ST AND 2ND ORDERS		3RD AND 4TH ORDERS	
<p>PROCESSES AND PROPERTIES INDEX</p> <p>CA</p> <p>10</p> <p>Acid saponification of butyl(3-chloroacetyl)acetic acid. G. T. Tatevnyan and M. A. Nikogonyan (Chem. Inst. Armenian Acad. Sci. S.S.R.). <i>Proc. Acad. Sci. Armenian S.S.R.</i> 1945, III, 15-19 (in Russian with English summary). — To a soln. of $\text{NaClBu}(\text{CO}_2\text{Et})$, prepd. from 15 g. Na and 140 g. $\text{BuCl}(\text{CO}_2\text{Et})$, in 160 g. abs. EtOH, there was added with cooling and stirring 81 g. 2,4-dichloro-2-butene, after which the mixt. was boiled for 3-4 hrs. After distn. of EtOH and acylation by HCl the org. layer was distd. to yield 83.1% di-<i>Et</i> butyl(3-chloroacetyl)malonate, b_p 130-5°, d_4^{20} 1.0500, n_D^{20} 1.4587. Hydrolysis by refluxing for 3-4 hrs. with alc. NaOH gave 90%; butyl(3-chloroacetyl)malonic acid, m. 120° (from water). (Heating this over a free flame, followed by distn. in vacuo, gave 90.1% butyl(3-chloroacetyl)acetic acid, b_p 134-5°, d_4^{20} 1.0417, n_D^{20} 1.4671. The above (15 g.) was treated with cooling with 18.7 cc. concd. H_2SO_4 and was allowed to stand at room temp. for 2 days to yield 85.9% α-butyl-γ-acetylbutyric acid, b_p 147-9°, d_4^{20} 1.0102, n_D^{20} 1.4520; semicarbazone, m. 139-40° (from water). G. M. Kosolapoff</p>			
<p>ASACSLA METALLURGICAL LITERATURE CLASSIFICATION</p>			

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Synthesis of polycyclic hydroaromatic ketones. 1. 3-Keto-1,2,3,9,10,11-hexahydrophenanthrene. G. T. Tatevnyan and A. G. Vardanyan. *Proc. Acad. Sci. Armenian S.S.R.* 4, No. 3, 71-6 (1948).--The $\text{PhCH}_2\text{CH}_2\text{CNa}(\text{CO}_2\text{Et})$, from 44.2 g. $\text{PhCH}_2\text{CH}_2\text{CH}(\text{Cl})\text{H}$, in 85 cc. EtOH and 26 g. $\text{MeCCl}_2\text{CHCl}_2$ refluxed 3.5 hrs. yield 79.24% *di-Et phenethyl(3-chloroacetyl)malonate*, b_p 202-7° (on redistn. b.p. 205-7°, d₄²⁰ 1.1137, n_D²⁰ 1.5030). This (44.4 g.) refluxed 2.5 hrs. with 15 g. NaOH and 220 cc. aq. EtOH gave 80% *β-phenethyl(3-chloroacetyl)malonic acid*, m. 164-5° (from dil. EtOH). On heating this gave 95% *α-(3-chloroacetyl)-γ-phenylbutyric acid*, b. 203-4°, d₄²⁰ 1.1290, n_D²⁰ 1.5295. Treatment of this in the cold with 10 vols. H_2SO_4 (d. 1.84) followed by gradual heating to 60-70° in a N atm. for 2.5 hrs., gave 74.9% 3-keto-1,2,3,9,10,11-hexahydrophenanthrene, m. 80° (from aq. EtOH). G. M. Kosolapoff

157 AND 158 ORDERS PROCESSES AND PROCESSES NOTES		159 AND 160 ORDERS PROCESSES AND PROCESSES NOTES	
<div style="position: absolute; top: 10px; left: 10px; font-size: 2em;">Ca</div>		<div style="position: absolute; top: 10px; right: 10px; font-size: 2em;">10</div>	
<p style="text-align: center;">Sulfuric acid hydrolysis of phenyl(3-chlorocrotyl)acetic acid. G. T. Tatevosyan and A. G. Vardanyan. <i>Proc. Acad. Sci. Armenian S. S. R.</i> 4, No. 4, 97-101(1946).-- The $\text{PhCNa}(\text{CO}_2\text{Et})$, from 118 g. $\text{PhCH}(\text{CO}_2\text{Et})$, 11.5 g. Na, and 130 g. abs. EtOH, and 74 g. $\text{MeCCl}:\text{CHCl}:\text{Cl}$ refluxed 6 hrs. yielded 76% di-Et phenyl(3-chlorocrotyl)malonate, b_p 100-5°, d₄²⁰ 1.1322, n_D²⁰ 1.5100. From 100.5 g. of the ester refluxed with 42 g. NaOH and 260 cc. EtOH 4 hrs., treated with 150 cc. water, then distd. to remove the bulk of the EtOH, and acidified with HCl, there was obtained 91.45% phenyl(3-chlorocrotyl)acetic acid, as a viscous green oil, d₄²⁰ 1.1724, n_D²⁰ 1.5422, b_p 102-5°, which crystd. on long standing, m. 55-6°. This (11 g.) was treated with stirring and cooling with 60 cc. 85% H_2SO_4; when the reaction subsided, the mixt. was allowed to stand overnight, then treated with ice-water and extd. with Et₂O; removal of the Et₂O and rubbing of the residue with benzene gave 46.7% α-phenyl-γ-acetylbutyric acid, m. 35-6° (from benzene); <i>semicarbazone</i>, m. 160° (from EtOH). This result indicates that the presence of the carboxylic acid group in the α-position of the side chain hinders the normally expected cyclization during the H_2SO_4 treatment; the expected product was 1-methyl-3,4-dihydro-4-naphthoic acid. G. M. K</p>			
ASS-3LA METALLURGICAL LITERATURE CLASSIFICATION			
157 AND 158 ORDERS PROCESSES AND PROCESSES NOTES		159 AND 160 ORDERS PROCESSES AND PROCESSES NOTES	

FATEVOSYAN, G.T.; BABAYAN, G.T.

Synthesis of Heptene-2-carboxylic acid-5. Dokl.AN Arm. SSR 6 no.2:
47-50 '47. (MLRA 9:8)

1. Khimicheskiy institut Akademii nauk Armyanskoy SSR, Yerevan.
Predstavleno S.P. Gambaryanom.
(Heptene carboxylic acid)

CA

Synthesis of substituted γ -acetylbutyric acids. G. T. Tatevosyan and M. O. Melikyan (Chem. Inst. Armenian SSR Acad. Sci.), *J. Gen. Chem. (U.S.S.R.)* 17, 975-80 (1947). — Di-Et butyl(3-chloro-2-butenyl)malonate, b_p 130-5°, d₄²⁰ 1.0500, n_D²⁰ 1.4587, was prepd. in 82% yield by addn. of 81 g. CICH₂CH:CClMe slowly to BuCNa·BuCH(CO₂Et)₂ (from 15 g. Na, 168 g. abs. EtOH, and 140 g. the EtOH, addn. of dil. HCl to dissolve the NaCl ppt., sepn. of the org. layer, and extrn. of the aq. layer with (CH₂Cl)₂). The ester (60 g.), 23.9 g. NaOH, and 360 cc. 95% EtOH were refluxed 3 hrs., dild. with 100 cc. H₂O, and freed of EtOH by distn.; the cooled mixt., treated with 90 g. 25% HCl and filtered, gave 66.07% MeCCl:CHCH₂CBu(CO₂H), m. 129° (from H₂O). The latter (28.1 g.) heated on a free flame, followed by distn., gave 80.1% butyl(3-chloro-2-butenyl)acetic acid, b_p 134-0°, d₄²⁰ 1.0417, n_D²⁰ 1.4671, a viscous oil, insol. in H₂O. This (15 g.) was treated, with ice cooling and stirring, with 18.7 g. concd. H₂SO₄ and the mixt. was allowed to stand 2 days with occasional shaking; on cooling and addn. of 25 cc. H₂O and 18.7 g. K₂CO₃, followed by extrn. with Et₂O and distn., there was obtained 85.9% α -butyl- γ -acetylbutyric acid, b_p 147-9°, d₄²⁰ 1.0102, n_D²⁰ 1.4525, semicarbazone m. 139-40° (from H₂O). CICH₂CH:CClMe (74.32 g.) with iso-AmCNa(CO₂Et)₂ (from 13.7 g. Na, 136.75 g. iso-AmCH(CO₂Et)₂, and 154 g. abs. EtOH) gave 70.3% di-Et isoamyl(3-chloro-2-butenyl)malonate, b_p 158-60°, d₄²⁰ 1.0322, n_D²⁰ 1.4550. This (3 g.), hydrolyzed by 3 g. KOH in 25 cc. H₂O, gave 52% isoamyl(3-chloro-2-butenyl)malonic acid, m. 145-6° (from

H₂O), insol. in cold H₂O. Thermal decompn. of this gave 80.3% isoamyl(3-chloro-2-butenyl)acetic acid, b_p 143-4°, m. 22-4°. This (8.25 g.) was hydrolyzed by 9.6 cc. concd. H₂SO₄, as described above, to give 80.4% α -isoamyl- γ -acetylbutyric acid, b_p 170°, d₄²⁰ 0.9902, n_D²⁰ 1.4513; semicarbazone m. 152-4° (from water). CICH₂CH:CClMe (68 g.) with PhCH₂CNa(CO₂Et)₂ (from 117.7 g. PhCH₂CH(CO₂Et)₂, 11 g. Na, and 120 g. EtOH) gave 90.1% di-Et benzyl(3-chloro-2-butenyl)malonate, b_p 185-6°, d₄²⁰ 1.1175, n_D²⁰ 1.5002. This (50 g.) was hydrolyzed by 18 g. NaOH in 250 cc. EtOH to give 42.27% benzyl(3-chloro-2-butenyl)malonic acid, m. 142-3° (from H₂O). Thermal decompn. gave 84.43% benzyl(3-chloro-2-butenyl)acetic acid, b_p 195-7°, d₄²⁰ 1.1361, n_D²⁰ 1.5265 (oxidation by alk. KMnO₄ at room temp. gave benzylsuccinic acid, m. 158-60°); 8 g. of this with 6 cc. 84.5% H₂SO₄ gave 85.64% α -benzyl- γ -acetylbutyric acid, m. 63-4°, b_p 192-5°; semicarbazone m. 153-5° (from EtOH).

G. M. Kosolapoff

TATEVOSSIAN, G. T.

Tatevossian, G. T., and Melikian, M. C.-^{*} The Synthesis of Substituted
y-Acetylbutyric Acids" (p. 980)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1947, Vol. 17, No. 5

CA 10

Isomeric transformations of methycyclobutylcarbinol.
 G. I. Tatevosyan, M. O. Melikyan, and A. T. Terzyan.
J. Gen. Chem. (U.S.S.R.) 17, 981-6 (1947).—The sole
 product of dehydration of methycyclobutylcarbinol (I)
 by means of CrO_3 is 1-methylcyclopentene;
 the same product is formed also by dehydrohalogenation
 of the bromide of the carbinol by quinoline. I was prepd.
 by reduction of acetylcyclobutane (from the vapor re-
 action of AcOH and cyclobutanecarboxylic acid over MnO)
 at $410-20^\circ$ with Na in moist Et_2O : I, bp $136-9^\circ$, d_4^{20}
 0.8074 , n_D^{20} 1.4443 . I (12.7 g.) heated with 30 g. CrO_3
 (CO_2H), in a distn. flask gave 43.3% 1-methylcyclopen-
 tene, bp $70-1^\circ$, d_4^{20} 0.7801 , n_D^{20} 1.4344 , which instantly
 decolorizes KMnO_4 and Br water and on oxidation by
 KMnO_4 gives γ -acetylbutyric acid (hydrate, m. $34-6^\circ$;
 semicarbazone monohydrate, m. $167-9^\circ$). I (7 g.)
 was treated with cooling with 30 cc. HBr satd. at 0° ;
 after standing 24 hrs., the mixt. was boiled 25-30 min.,
 cooled, dild. with H_2O , and extd. with Et_2O to give
 61.5% I bromide, bp $74-6^\circ$, d_4^{20} 1.3004 , n_D^{20} 1.4823 ,
 which acquires a blue-violet color on standing. Heating
 17 g. bromide with 25 g. quinoline to $120-30^\circ$, and finally
 to $190-200^\circ$, gave 79.2% 1-methylcyclopentene.
 G. M. Kosolapoff

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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CA

10

Synthesis of polycyclic hydroaromatic ketones. 1.
p-Keto-1,2,3,9,10,10a-hexahydrophenanthrene. (1). T.
Sisoyan and A. O. Vardanyan. *Zhur. Obshch. Khim.*
(Gen. Chem.) 17, 1828-32 (1947).—See C.A. 41, 432a.
E. J. C.

5-Allyl-5-(3-chloro-2-butenyl)barbituric acids. G. T. Tatevosyan and M. T. Tuteryan. *Zhur. Priklad. Khim.* (J. Applied Chem.) 20, 287-92 (1947).—MeCCI:CHCl₂:CH₂(CO₂Et)₂ (I), prepd. in 71.8% yield from MeCCI:CHCl₂:Cl and CH₂(CO₂Et)₂, colorless oil, b_p 135-7°, n_D²⁰ 1.4541, d₄²⁰ 1.0713. To 5 g. Na in 50 ml. hot EtOH were added 8.5 g. dry urea and 27.8 g. I in 65 ml. warm EtOH, the mixt. heated 2 hrs. at 70-80°, refluxed 6 hrs. longer, the EtOH distd. off, the sirupy residue taken up with 50 ml. H₂O, and 30 ml. concd. HCl added; the thick oil which sepd. solidified on standing and after several recrystals. (dil. EtOH) yielded 13 g. (53.18%) 5-ethyl-5-(3-chloro-2-butenyl)barbituric acid, has a bitter taste, m. 149-50°, is readily sol. in EtOH, acetone, alkalies, and hot water, insol. in cold water. The corresponding iso-Am deriv., obtained in 62.25% yield, m. 125-7°. Di-Et allyl(3-chloro-2-butenyl)malonate (II) (from allylmalonic ester), b_p 132-4°, d₄²⁰ 1.0670. 5-Allyl-5-(3-chloro-2-butenyl)barbituric acid (33.7% from II) m. 174-5°. Di-Et bis(3-chloro-2-butenyl)malonate (III) (C.I. 30, 1484) (79.6%¹), b_p 178-80°, b_p is 191-3°, d₄²⁰ 1.1437, n_D²⁰ 1.4904. 5,5-Bis(3-chloro-2-butenyl)barbituric acid (82% from III), colorless crystals, m. 160-70°, insol. in hot water, and more difficultly sol. in org. solvents; the acid was hydrolyzed to bis(3-chloro-2-butenyl)malonic acid (IV) by boiling 10¹/₂ hr. with NaOH, also obtained by the hydrolysis of III. Bis(3-chloro-2-butenyl)acetic acid was obtained by heating 7.9 g. IV to 170-80°; the rapid evolution of CO₂ was completed in 5-10 min., and the residue on distn. in vacuo yielded 5.81 g. (87.2%) of a sticky liquid, m. 37-8°, d₄²⁰ 1.1629, n_D²⁰ 1.4992 (supercooled liquid). Preliminary tests indicated that these acids were very toxic, but not hypnotic; 0.5-1.5 g. caused strong excitation, convulsions, and death to dogs. H. G.

CROSS ELEMENTS		OPEN		MATERIALS INDEX		PROCESS AND PROPERTIES INDEX	
<p>Polycyclic hydroaromatic ketones. II. 3-Keto-7-methyl-1,2,3,9,10,10a-hexahydrophenanthrene. G. T. Tatevnyan and A. G. Vardanyan. <i>Zhur. Obshchei Khim.</i> (J. Gen. Chem.) 19, 327-31 (1949). Cf. C.I. 41, 432a.</p> <p>3-MeC₁₂H₁₁CH₂CH₂OH (107.5 g.), 342 g. 48% HBr, and 100 g. H₂SO₄ boiled 3.5 hrs. gave 76.3% 3-MeC₁₂H₁₁CH₂CH₂Br, b₈₈ 90°. This (120 g.) was added to NaCH₃(CO₂Et) (from 145 g. malonic ester) in 290 ml. EtOH, let stand 0.5 hr., refluxed 3 hrs., let stand overnight, and acidified with HCl after concn., to yield 85% 3-MeC₁₂H₁₁CH₂CH₂CH₂CO₂Et, b₁₅₀ 2°; d₄ 1.0544, n_D 1.4900. This (120 g.) treated with 11 g. Na in 200 ml. EtOH, followed by addn. with cooling of 65 g. CCl₄, CH₃CCl₃, and 12.7 g. MeCCl₂CH₂CH₂CH₂CO₂Et, b₁₉₁ 4°, d₄ 1.0974, n_D 1.5000. This (80 g.) refluxed 1 hr. with 30 g. NaOH and 110 ml. EtOH, treated with 200 ml. H₂O, concd., and acidified with 130 g. HCl gave 76% of the free acid, m. 155-6° (from H₂O). Heating in a Claisen flask gave 94% (3-MeC₁₂H₁₁CH₂CH₂CH₂CO₂Et), b₁₉₃ 0°. This (21 g.) treated with ice cooling with 115 ml. H₂SO₄ (d. 1.8), let stand 0.5 hr., and heated 5 hrs. to 70-85°, gave, after ice treatment and washing with alkali 60.9% 3-keto-7-methyl-1,2,3,9,10,10a-hexahydrophenanthrene, m. 95-6° (from EtOH); semi-arabazone, m. 221-2° (from benzene); oxime, m. 161-2° (from C₆H₆). The ketone (5.97 g.) heated 3.5 hrs. with 4.5 g. Se at 200-320° (finally 350°), then</p>							
<p>boiled 20 min. with 10% NaOH, and the insol. part allowed to crystallize, gave 0.50 g. 3-methylphenanthrene, m. 54-5° (pure, m. 117-18°), while the alk. soln., after extr. with benzene and acidification with HCl, gave 2.73 g. 3-hydroxy-7-methylphenanthrene, b₂₀₀ 1°, m. 140-7° (from EtOH); pure, m. 151-6° (decompos.); heating with Zn dust to red heat gave 2-methylphenanthrene.</p> <p>III. 3-Keto-1,2,3,11,12,12a-hexahydrochrysene. Ibid.</p> <p>III. 3-Keto-1,2,3,11,12,12a-hexahydrochrysene. Ibid.</p> <p>332-6.—Reduction of 1-C₁₂H₉CH₂CO₂Et with Na-EtOH gave 61% tetrahydro-1-naphthalenethanol, b₁₅₇ 8-5°, d₄ 1.0040, n_D 1.5033. This (0.42 g.) and 5.70 g. Se heated to 300-20° 5 hrs. gave 2.45 g. of a hydrocarbon, b₂₅₀ 5° (pure, m. 98°), which was apparently 1-C₁₂H₉CH₂CH₂CH₂CO₂Et, the use of S instead of Se, 4 hrs. at 180-20° EtOH, gave 60% 1-C₁₂H₉CH₂CH₂CH₂CO₂Et, b₁₅₂ 4°, this with NaCH₃(CO₂Et) gave 1-C₁₂H₉CH₂CH₂CH₂CH₂CO₂Et, b₂₁₃ 15°, which on treatment with Na in EtOH followed by CCl₄, CH₃CCl₃, as described above (preceding part) gave 88% (1-C₁₂H₉CH₂CH₂CH₂CH₂CH₂CO₂Et), b₂₁₃ 1°, d₄ 1.1298, n_D 1.5300. Refluxing 65 g. of this with 10 g. NaOH in 200 ml. EtOH gave 55.95% free acid, m. 108.5-9° (from C₆H₆-Me₂CO), which on heating with a free flame gave (1-C₁₂H₉CH₂CH₂CH₂CH₂CH₂CH₂CO₂Et), m. 80-7° (from dil. EtOH). This (0 g.) and 180 g. 84.5% H₂SO₄ warmed 1.5 hrs. to 60-5° gave, after standing overnight and treatment with ice, 78.6% 3-keto-1,2,3,11,12,12a-hexahydrochrysene, m. 187-7.5° (from C₆H₆-EtOH); oxime, m. 210° (from C₆H₆-EtOH).</p>							
G. M. Kosolapoff							
<p>ASB-36A DETALLURGICAL LITERATURE CLASSIFICATION</p> <p>130000 SYNTHESE</p> <p>181000 HIGHER CHEMISTRY</p> <p>REVISIONS</p> <p>130000 HIGHER CHEMISTRY</p> <p>181000 HIGHER CHEMISTRY</p>							

1481
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 10
 Synthesis of 1-methyl-4-alkyl-1-cyclohexen-3-ones. M. O. Melikyan and G. T. Tatevosyan, *Zhur. Obshch. Khim.* (J. Gen. Chem.) 21: 696-703 (1951). To the Na-deriv. of $\text{AcCH}(\text{CHMe})\text{CO}_2\text{Et}$ from 80 g. of the ester, 10 g. Na, and 114 g. abs. EtOH, was added with cooling 85.6 g. $\text{MeCCl}_2\text{CHCH}_2\text{Cl}$; acclification and extn. with C_6H_6 , after 3 days yielded 27.55% *Et* α -isopropyl- α -chloro- α -chloroacetate, (I), b. 124.7°, d_4^{20} 1.0715, n_D^{20} 1.4720; this (10.1 g.) treated, dropwise, with ice cooling, with 9.0 ml. H_2SO_4 (d. 1.78), let stand 2 days, and treated with 15.4 ml. H_2O and 15.7 g. Na_2CO_3 gave 63.1% 1-methyl-4-isopropyl-4-carbethoxy-1-cyclohexen-3-one, b. 141.4°, d_4^{20} 1.0008, n_D^{20} 1.4838 (cf. Walker, C. 1. 30, 1012°). A small amt. of 1-methyl-4-isopropyl-1-cyclohexen-3-one, b. 102.4°, also forms; this is obtained in 62% yield on refluxing the ester 12 hrs. with MeOH-KOH . The pure product, b. 111.11°, d_4^{20} 0.9415, n_D^{20} 1.4811 (ovine, m. 117.18°), is identical with naturally occurring *dl*-piperton. Oxidation by alk. KMnO_4 gives $\text{AcCH}_2\text{CH}_2\text{CH}(\text{CHMe})\text{CO}_2\text{H}$, isolated as the semicarbazone, m. 156.7°. Similarly the *dl* analog of I gave 72.5% *Et* α -butyl- α -chloro- α -chloroacetate, b. 107.0°, d_4^{20} 1.0000, n_D^{20} 1.4658, hydrolyzed by aq. H_2SO_4 as above to 62.7% 1-methyl-4-butyl-4-carbethoxy-1-cyclohexen-3-one, b. 111.5-12.5°, d_4^{20} 1.0155, n_D^{20} 1.4780, which on refluxing with MeOH-KOH gave 47.27% 1-methyl-4-butyl-1-cyclohexen-3-one, b. 95.6°, d_4^{20} 0.9314, n_D^{20} 1.4780 (semicarbazone, m. 180.2°); oxidation with KMnO_4 gives $\text{AcCH}_2\text{CH}_2\text{CH}(\text{CHMe})\text{CO}_2\text{H}$, isolated as the semicarbazone, m. 139.10°. *iso*-Am CHAcCO_2Et similarly gave 53.2% *Et* α -isopropyl- α -chloro- α -chloroacetate, b. 116.18°, d_4^{20} 1.0262, n_D^{20} 1.4612, hydrolyzed to 55.5% 1-methyl-4-isopropyl-4-carbethoxy-1-cyclohexen-3-one, b. 112.15°, d_4^{20} 1.0015, n_D^{20} 1.4768, which with KOH-MeOH gave 30.1% 1-methyl-4-isopropyl-1-cyclohexen-3-one, b. 81.0°, d_4^{20} 0.9100, n_D^{20} 1.4808. Similarly prepd. were 1: α -benzyl- α -chloro- α -chloroacetate (73.2%), b. 146.8°, d_4^{20} 1.1215, n_D^{20} 1.5202; 1-methyl-4-benzyl-4-carbethoxy-1-cyclohexen-3-one, (61.6%), b.p. unstated, m. 43.4° (from EtOH); 1-methyl-4-benzyl-1-cyclohexen-3-one (74%), b. 125.7°, d_4^{20} 1.0367, n_D^{20} 1.5511 (semicarbazone, m. 180.90° (from EtOH)). Oxidation gave $\text{AcCH}_2\text{CH}_2\text{CH}(\text{CHMe})\text{CO}_2\text{H}$, b. 180.5°, m. 61.5°, G. M. K.

TATEVOSYAN, G. T.

"Synthesis of polycyclic hydroaromatic ketones. IV. 3-Keto-6-methyl-1,2,3,9,10,11,-
hexahydrophenanthrene." G. T. Tatevosyan and A. G. Vardanyan. (p. 1170)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1951, Vol 21, No 6.

TATEVOSYAN, G. T.

"Synthesis of polynuclear hydroaromatic ketones. V. 3-Keto-7-methoxy-1,2,3,11,12,12a-hexahydrochrysene." G. T. Tatevosyan and S. A. Vardanyan. (p. 1238)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1951, Vol 21, No 7.

TATEVOSYAN, G. T., BABAYAN, V. G.

Benxophenanthrene

Synthesis of 3, 4-benzophenanthrene and its homologs. Zhur.ob.khim. 22 no. 8, 1952.

Monthly List of Russian Accessions, Library of Congress, November 1952. Unclassified.

TATEVOSYAN, G. T.

Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Organic Chemistry

Synthesis of polynuclear hydroaromatic ketones. VI.
2-Oxo-1,2,3,11,12-hexahydro-6,7-accechrysene S. A.
Vartanyan, P. A. Zorogin, and G. T. Tatevosyan. *Zhur.*
Obshch. Khim. 23, 829-34 (1953); cf. C.A. 46, 2037a,
8045f. — 5-Acenaphthenebutyric acid (C.A. numbering), m.
142-3°, (100 g.) refluxed in 500 ml. 90% EtOH and 25
ml. concd. H₂SO₄ 0 hrs. gave 00.9% *Et ester*, b_p 200-
2°, m. 39° (Fieser, *et al.*, C.A. 30, 0734). This
(70 g.) in Et₂O was added to the reaction mixt. from
6.1 g. Na (suspended in 150 ml. Et₂O), treated with 12.6 g.
EtOH in 50 ml. Et₂O and finally with 57 g. (CO₂Et)₂, and
the whole refluxed 20 hrs., treated with dil. H₂SO₄, extd.
with Et₂O, the Et₂O evapd., and the residue heated *in vacuo*
until all CO evolution stopped gave 67.5% *di-Et* [2-(5-
acenaphthenyl)ethyl]malonate, b_p 216-18°. This (170 g.)
added to 11.75 g. Na in 160 g. EtOH, followed by 75 g.
MeCCl:CHCl₂Cl, and the mixt. refluxed 0 hrs. gave,
after the usual treatment, 47.6% *di-Et* [2-(5-acenaphthenyl)-
ethyl](3-chloro-2-butenyl)malonate, b_p 230-2°, m. 46-7°
(from EtOH). This (112 g.) refluxed 0 hrs. with 31 g.
NaOH and 550 ml. 90% EtOH gave, after concn. and
acidification, 85.2% *free malonic acid*, m. 174-5° (from
C₆H₆), which, heated *in vacuo*, gave 76%. The α -(3-
chloro-2-butenyl)-5-crotyl- γ -acenaphthenebutyric acid, m. 114-
15° (from MeOH). This acid (10 g.) added to 75 g. H₂SO₄,
(d. 1.76), kept 0.5 hr., heated in a CO₂ atm. 40 min. to
50-5°, kept 3 hrs. at room temp., and quenched in ice,
gave 48.4% 1-oxo-2-(3-oxobutyl)-1,2,3,4-tetrahydro-8,9-
phenanthrene, m. 115-16° (from MeOH) (under more
drastic conditions the product is sulfonated), which (3 g.),
refluxed 4 hrs. with 40 ml. 20% NaOH, gave 67.6% 3-
oxo-1,2,3,11,12,12a-hexahydro-6,7-accechrysene, m. 184-5°
(from MeOH); 2,4-dinitrophenylhydrazones, m. 171-2°
(from EtOH-CHCl₃). This with 10% Pd-C in CO₂ at
280-300° gave in 4 hrs. 0.5 g. 6,7-accechrysene, m. 233-0°
(from C₆H₆-EtOH); the product cannot be sublimed with-
out decompn. Thus, despite the 4,6-ace bridge in the
naphthyl residue of the initial acid, which should favor
peri-cyclization, in this case α -cyclization took place. The
structures of the chrysene derivs. were confirmed by ab-

(over)

2/2 S. A. Vardanyan

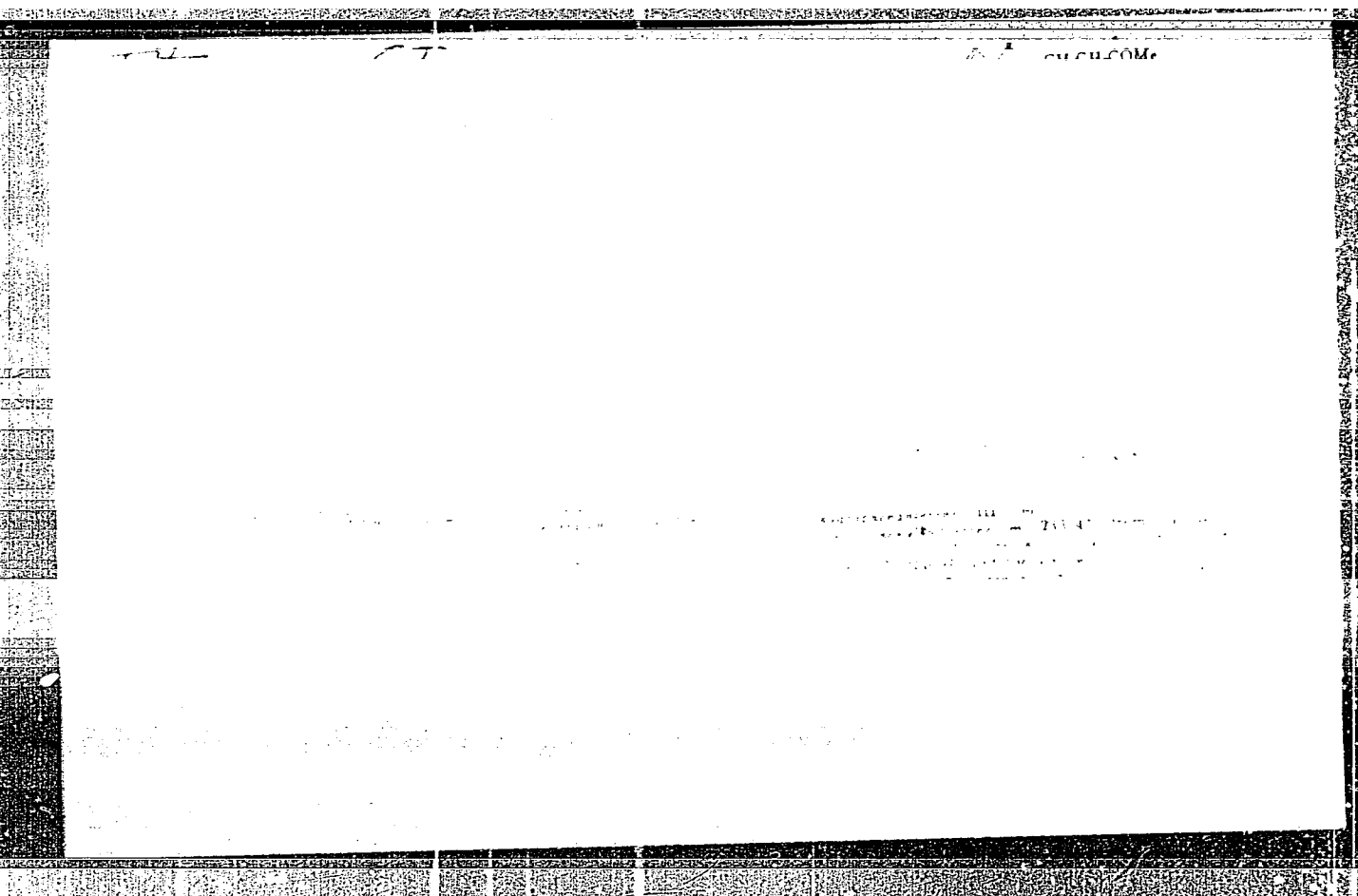
sorption spectra, by comparison with known data. 3-Methylchrysene, obtained by treatment of the oxo deriv. with MeMgI and dehydrogenation of the product, and 6,7-acechrysene have the same absorption max. (318-322, 306-310, 294-296, 283-287 mμ).

G. M. Kosolapoff

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BABAYAN, V.O.; TAGORETS, P.A.; TATEVOSYAN, G.T.

Synthesis of hydrocarbons of the 1,2-benzanthracene series. *Zhur.ob.*
khim. 23 no.7:1214-1220 J1 '53. (MLBA 6:7)

1. Khimicheskiy institut Akademii nauk Armyanskoy SSR.
(Benzanthracene series)

TATEVOSYAN, G. T.

USSR/Chemistry - Hydroaromatic ketones

Card 1/1 Pub. 151 - 26/37

Authors : Tatevosyan, G. T., and Vardanyan, A. G.

Title : Synthesis of polynuclear hydroaromatic ketones. Part 8.- 3-methyl- and 8-methoxy-3-keto-1,2,3,9,10,10a-hexahydrophenanthrenes

Periodical : Zhur. ob. khim. 24/10, 1845-1851, Oct 1954

Abstract : The effect of methyl and methoxyl groups oriented in ortho-position of the aromatic nucleus on the reaction of sulfuric acid hydrolysis and double cyclization of alpha-(3-chlorocrotyl)-gamma-phenyl butyric acids was investigated. The investigated conversion process was found to be not much affected by the methyl group and the yield of the conversion product is of the same order as the non-substituted ketone and its other methyl homologues. The presence of the methoxyl group in meta-position was found to be a deterrent in the conversion process. Six references: 3-USSR; 2-German and 1-USA (1923-1953).

Institution : Academy of Sciences Arm-SSR, Chemical Institute

Submitted : May 18, 1954

Tatevosyan, G. T.

6

Synthesis of polynuclear ketones. IX. 2-Oxo-2,4,4-trimethyl-6,7-hexahydro-5H-dibenzof[a]cycloheptatriene. C. 1, 1, 1, 1-tetrafluoroethane. G. T. Tatevosyan, S. G. Terzyan, S. A. Vardanyan, and A. A. (Engl. translation). See C.A. 50, 7097a. B. M. H.

M. A. YOUTZ

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Tatevosyan, G.T.

5

✓ Synthesis of polyunsaturated ketones. IX. 2-Oxo-2,3,4,4a-

6,7-hexahydro-5H-benzo[a,cycloheptatriene. G. T.

Tatevosyan, G. T., Terzian, S. A., Vardanyan and A. G.

Vardanyan, Zhur. Obshchei Khim. 25, 1766-71(1955); cf.

C.A. 44, 8345a, 49, 13 97; --Di-Et malonate and PhCH₂-

CH₂CH₂Br gave Ph(C₂H₅CH₂CO₂Et)₂ I, b, 170-3° d,

1.0546 n_D²⁰ 1.4901 I, 20 g. converted to Na deriv. with

10 g. Na in 160 ml. EtOAc, was treated with 55 g. Me-

CH₂CH₂Cl and the mix. refluxed 6 hrs., yielded 30.6%

PhCH₂CH₂CO₂Et, CH₂(H₂CClMe) II, b, 184-200° d,

1.0970, n_D²⁰ 1.5033. II, 131 g.) refluxed 4 hrs. with 43 g.

NaOH in 650 ml. 90% EtOH and acidified, gave 72% Ph-

CH₂CH₂CO₂H, CH₂CH₂CClMe, m. 124-5°, which heated

gave PhCH₂CH₂CO₂CH₂CH₂Cl, (III), b, 123-5°

m. 39-40° (n_D²⁰ 1.5288, supercooled). III treated with H₂SO₄

(d. 1.78) at 60° under CO₂, gave no ketonic material; at

room temp. the results were also neg., both the H₂SO₄ and

the polyphosphoric acid methods being unsatisfactory for

ring closure. III (9 g. was treated with 7.1 g. PCl₅ in

dry CCl₄ and the product treated with 40 cc. SnCl₄ in 150 ml

CCl₄ and refluxed 6 hrs. After washing with HCl and

NaOH, there was obtained 3.4 g. neutral product, identi-

fied as crude 2-(4-chlorocarbonyl)benzosuberone (IV). IV

3.4 g. treated with 11 ml. H₂SO₄ (d. 1.78) and kept 2 days

at 15° gave after treatment with ice and washing with

water 1.1 g. 2-(4-chlorocarbonyl)benzosuberone (V), m. 140-1° from Et-

2OAc, benzene, orange-red, m. 183-5°. To 5.7 g.

Na in 150 ml. dry MeOH was added 65 ml. dry CCl₄ and

10.5 g. 2-carbomethoxybenzosuberone, after refluxing 3.5

hrs. the mixt. was cooled, treated with 31.5 ml. MeCO-

CH₃ (d. 1.36) and refluxed 1.5 hr. to yield 15 g. 2-(4-chloro-

carbonyl)benzosuberone, which hydrolyzed

by refluxing 3 hrs. with 26.5 g. NaOH in 45 ml. H₂O and

185 ml. MeOH, gave IV, a dark oil, in 98.8% yield. IV

cyclized with H₂SO₄, as above at room temp. yielding 56.3%

V, m. 100-1°

G. M. Kosolapov

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Name TATEVOSYAN, Gurgan Tigranovich

Dissertation Study in the Field of the Synthesis of
Polynuclear Hydroaromatic Ketones

Degree Doc Chem Sci

Affiliation Chem Inst, Acad Sci Ar SSR

Defense Date, Place 1 Mar 56, Council of the Inst of Organic
Chemistry imeni Zelinskiy, Acad Sci USSR

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*Tatevosyan
ARM SSR*

Tatevosyan, G. T.

Call Nr: AF 1135663

AUTHOR: None given

TITLE: Syntheses of Heterocyclic Compounds (Sintezy geterotsiklicheskikh soyedineniy)

PUB. DATA: Izdatel'stvo AN Armyanskoy SSR, Yerevan, 1956, 84 pp., 2000 copies Armyanskoy

ORIG. AGENCY: Akademiya nauk/SSR. Institut tonkoy organicheskoy khimii

EDITOR: A. L. Mndzhoyan, Editor-in-Chief
Editorial Staff: Aroyan, A. A., Afrikyan, V. G., Babiyan, N. A., Mndzhoyan, O. L., Tatevosyan, G. T.

PURPOSE: The purpose of this book is to facilitate the work of scientists engaged in the preparation of compounds frequently used as initial substances.

COVERAGE: The Institute of Fine Organic Chemistry of the Academy of Sciences of the Armenian SSR is publishing new series of methods for the synthesis of heterocyclic compounds. Not only methods developed by the Institute, but also methods developed by other institutions will be included. All the published methods will be tested at the Institute

Card 1/25

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Syntheses of Heterocyclic Compounds (Cont.)

of Fine Organic Chemistry of the Academy of Sciences of the Armenian SSR. Because of the great interest in furan derivatives as raw material for many intermediates and for products used in medicine and agriculture, this issue is devoted to the synthesis of furan derivatives exclusively. The description of "Methods" covers the literature up to 1956. The description of "Other Methods of Preparation" covers the literature up to 1954. Names of scientists concerned with the development and testing of the methods are in the abstracts of the individual methods.

Page

Synthesis of 5-benzyl-furan-2-carboxylic acid: Proposed 11
by A. L. Mndzhoyan and V. G. Afrikyan; verified by
G. T. Tatevosyan and N. M. Divanyan. The product was prepared from methyl ester of 5-benzylfuran-2-carboxylic acid and a 10% NaOH solution by heating the mixture on a water bath for 3-4 hrs. M.p. 104-105°C; yield, 84.1-89.1%. The authors state that H. J. H. Fenton and F. Robinson (1909) prepared a substance which they assumed to be 5-benzylfuran-2-carboxylic acid by condensation of 5-chloromethyl-furfural

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Syntheses of Heterocyclic Compounds (Cont.)

Page

with benzene followed by oxidation of the aldehyde formed. However, this product had a m.p. of 167-169°C; thus it could not be 5-benzylfuran-2-carboxylic acid. Three references, one Slavic (1953).

Synthesis of 3-(5'-benzyl-2'-furyl)-5-mercapto-1,2,4-triazole: Proposed by A. L. Mndzhoyan and V. G. Afrikyan; verified by N. A. Babiyan and A. A. Dokhikyan. The product was obtained by heating a mixture of 5-benzyl-2-furoyl-thiosemicarbazide, sodium methylate, and methyl alcohol in an autoclave at 145-150°C for 3 hrs. M.p. 232°C; yield, 83.6-87.6%. One Slavic reference (1953).

13

Synthesis of 5-bromofuran-2-carboxylic acid: Proposed by A. L. Mndzhoyan and V. G. Afrikyan; verified by M. G. Grigoryan and Yu. O. Martirosyan. A mixture of furan-2-carboxylic acid, red phosphorus and chloroform is heated to boiling on a water bath, and bromine is added dropwise over a period of 5-6 hrs. The solvent is

15

Card 3/25

Cell Nr: AF 1135663

Syntheses of Heterocyclic Compounds (Cont.)

Page

removed by distillation, water is added, and the mixture is heated for 3-4 hrs. After cooling and adding a 20% ammonia solution to strong alkaline reaction, BaCl₂ and bone black are added, and the mixture is heated to boiling for 30-40 min. M.p., 182-83°C; yield, 63.1-63.5%. Other methods of preparation: 5-Bromofuran-2-carboxylic acid may be obtained by bromination of ethyl ester of pyromucic acid dissolved in acetic acid, followed by hydrolysis of the obtained product by alcoholic alkali solution or by oxidation of 5-bromofurfural. The product can also be obtained by bromination of pyromucic acid with or without solvents (such as acetic acid, diethyl ether, chloroform, and carbon tetrachloride). Higher yields were obtained when the reaction was conducted in the presence of red phosphorus. Seven references, one Slavic (1946).

Synthesis of furfural diacetate: Proposed by V. G. Afrikyan and A. A. Dokhikyan. Freshly distilled furfural is slowly added to a mixture of acetic anhydride

18

Card 4/ 25

Call Nr: AF 1135663

Syntheses of Heterocyclic Compounds (Cont.)

Page

and conc. H_2SO_4 at $10^\circ C$. In 20-30 min., the temperature of the mixture reaches room temperature; sodium acetate is added, and the mixture is distilled in vacuo. The $140-142^\circ/20$ mm fraction is collected; yield 65-70%. Other methods of preparation: furfural diacetate can be obtained from furfural and acetic anhydride in the presence of sulfuric acid, zinc chloride, tin chloride, acetic acid, and other catalysts. Six references, none Slavic.

Synthesis of 5-diethylaminomethylfuryl-2-carbinol: Proposed by A. L. Mndzhoyan and M. T. Grigoryan; verified by N. A. Babiyan and N. M. Ogandzhanyan. Methyl ester of 5-diethylaminomethylfuran-2-carboxylic acid is added to lithium aluminum hydride. The mixture is allowed to stand overnight and the excess of lithium aluminum hydride is decomposed by addition of water. After filtration, drying, and vacuum-distillation, the $120-122^\circ/1$ mm fraction is collected. Yield, 80.2-83.5%. Three references, one Slavic (1953).

20

Card 5/25

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Syntheses of Heterocyclic Compounds (Cont.)

Page

Synthesis of methyl ester of 5-benzylfuran-2-carboxylic acid: Proposed by A. L. Mndzhoyan, V. G. Afrikyan, and A. A. Dokhikyan; verified by G. T. Tatevosyan and N. M. Divanyan. Anhydrous aluminum chloride is slowly added to a benzene solution of methyl ester of 5-chloromethylfuran-2-carboxylic acid. The mixture is heated for 4-5 hrs., at 80-85°C, cooled, and dilute HCl is added in order to dissolve the formed $Al(OH)_3$. After removal of the solvent by distillation, the product is distilled in vacuo, and the 150-155°/1 mm fraction is collected. Yield, 62.3-63.8%. On cooling, the product crystallizes; m.p. 43-44°C. One Slavic reference (1953).

22

Synthesis of methyl ester of 5-bromomethylfuran-2-carboxylic acid: Proposed by A. L. Mndzhoyan and V. G. Afrikyan; verified by G. T. Tatevosyan and S. G. Agbalyan. A rapid stream of hydrogen bromide is passed through a mixture consisting of methyl ester of furan-2-carboxylic acid, dry dichloroethane, paraformaldehyde, and zinc chloride. The reaction time is 2.0-2.5 hrs.; reaction temperature, 24-26°/2.5 mm; yield, 78.9-79.9%.

Card 6/25

Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

The crystallized product melts at 32-36°C. One Slavic reference (1953).

Synthesis of methyl ester of 5-butylmercaptomethylfuran-2-carboxylic acid: Proposed by A. L. Mndzhoyan and N. M. Divanyan; verified by O. L. Mndzhoyan and E. R. Bagdasar'yan. Toluene is added to metallic sodium and the mixture is heated with stirring until sodium is dissolved. Freshly distilled n-butylmercaptan is added dropwise, with continuous stirring, at 40-50°C., and the mixture is allowed to stand for several hours. Methyl ester of 5-chloromethylfuran-2-carboxylic acid is added dropwise to the mixture (2.0-2.5 hrs.), and the mixture is heated for 2 hrs. at 90-95°C. After removal of the solvent, the product is distilled in vacuo, and the 153-155°/4 mm fraction is collected. Yield, 89.1-92.9%. One Slavic reference (1953).

26

Card 7/25

Call Nr: AF 1135663

Syntheses of Heterocyclic Compounds (Cont.)

Page

Synthesis of methyl ester of 5-diethylaminomethylfuran-2-carboxylic acid: Proposed by A. L. Mndzhoyan, V. G. Afrikyan, and M. T. Grigoryan; verified by U. L. Mndzhoyan and O. Ye. Gasparyan. A benzene solution of diethylamine is added to a benzene solution of methyl ester of 5-chloromethylfuran-2-carboxylic acid. The mixture is heated to boiling for 4-5 hrs, cooled, and treated with a 10% HCl solution. Methyl ester of 5-diethylaminomethylfuran-2-carboxylic acid is obtained with a yield of 85.3-94.7%; b.p. 102-103°/1.5 mm. The same method may be applied to synthesize ethyl, propyl, isopropyl, butyl, and isobutyl esters of 5-dimethyl-, diethyl-, dipropyl-, and dibutylaminomethylfuran-2-carboxylic acids with similar yields. One Slavic reference (1953).

28

Synthesis of methyl ester of 5-methylfuran-2-carboxylic acid: Proposed by A. L. Mndzhoyan, V. G. Afrikyan, and M. T. Grigoryan; verified by G. T. Tatevosyan and S. G. Agbalyan. Zinc dust is added to a mixture of methyl ester of 5-chloromethylfuran-2-carboxylic acid and acetic

30

Card 8/25

Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

acid (90%) over a period of 2.0-2.5 hrs. The mixture is then heated with stirring for 20 hrs. The b.p. of the obtained product is 97-99°/12 mm; yield, 81-83%. Other methods of preparation are mentioned: 5-Methylfuran-2-carboxylic acid was also obtained by esterification of the acid prepared by oxidation of 5-methylfurfural with silver oxide. Three references, 1 Slavic (1953).

Synthesis of methyl ester of 5-propoxymethylfuran-2-carboxylic acid: Proposed by V. G. Afrikyan and G. L. Papayan; verified by O. L. Mndzhoyan and O. Ye. Gasparyan. Metallic sodium is dissolved in propyl alcohol and freshly distilled methyl ester of 5-chloromethylfuran-2-carboxylic acid is added dropwise to the solution. The mixture is heated to boiling for 8 hrs; the separated 5-propoxymethylfuran-2-carboxylic acid has a b.p. of 146-148°/5 mm; yield 76.7-78.4%. Two references, 1 Slavic (1953).

32

Card 9/25

Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AP 1135663

Page

34

Synthesis of methyl ester of furan-2-carboxylic acid:
Proposed by V. G. Afrikyan and M. T. Grigoryan; verified
by G. T. Tatevosyan and S. G. Agbalyan. Method I. A
rapid stream of hydrogen chloride is passed through a
boiling solution of furan-2-carboxylic acid in methyl
alcohol over a period of 2.5-3.0 hrs. The obtained methyl
ester of furan-2-carboxylic acid has a b.p. of 176-177°/680 mm;
yield, 79.3-81.6%. Method II. Conc. sulfuric acid is
added to a mixture of furan-2-carboxylic acid in methyl
alcohol. The mixture is heated to boiling for 4 hrs. The
yield of methyl of methyl ester of furan-2-carboxylic acid
obtained by Method II is lower than that obtained by method I
(79.3-81.6% and 75.4-76.2% resp.). Other methods of prepa-
ration: Methyl ester of furan-2-carboxylic acid may also
be obtained by esterification of the acid; methylation of
the acid with dimethyl sulfate in alkaline medium; reaction
of furoyl chloride with magnesium methylate in methyl
alcohol. Four references, none Slavic.

Card 10/25

Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

36

Synthesis of methyl ester of 5-chloromethylfuran-2-carboxylic acid: Proposed by A. L. Mndzhoyan and M. T. Grigoryan; verified by G. T. Tatevosyan and S. G. Agbalyan. A rapid stream of hydrogen chloride is passed through a mixture of methyl ester of furan-2-carboxylic acid, dichloroethane, paraformaldehyde, and zinc chloride. Reaction time, 2 hrs.; reaction temperature, 24-26°C. The obtained methyl ester of 5-chloromethylfuran-2-carboxylic acid has a m.p. of 34-36°C; yield; 80.7-81.9%. Other methods of preparation: chloromethylation of methyl ester of pyromucic acid in dichloromethane with paraformaldehyde and hydrogen chloride in the presence of zinc chloride; chloroform may be used instead of dichloromethane; phosphoric acid, aluminum chloride or a mixture of tin chloride hexahydrate with sodium sulfate may be used instead of zinc chloride. Ethyl, propyl, isopropyl,

Card 11/ 25

Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

butyl, and isobutyl esters of 5-chloromethylfuran-2-carboxylic acid were obtained by the same method with yields of 80-90%. Four references, 1 Slavic (1953).

Synthesis of 2-methylfuran (sylvan): Proposed by A. L. Mndzhoyan and G. T. Tatevosyan; verified by V. G. Afrikyan and G. L. Papayan. 5-Methylfuran-2-carboxylic acid is decomposed by heating at 170-175°C. The sylvan formed has a b.p. of 61°/680 mm; yield, 80.1-84.8%. Other methods of preparation: Dry distillation of wood; catalytic hydrogenation of furfural over catalysts (Cu or Cu-Cr) at temperatures >200°C, a mixture of furfural, furan, and sylvan is obtained by passing furfuryl alcohol over aluminum oxide at 390°C or heating it with a nickel catalyst at 150°C. Six references, 1 Slavic (1939).

39

Card 12/25

Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

42

Synthesis of 5-methylfuran-2-carboxylic acid: Proposed by A. L. Mndzhoyan and M. T. Grigoryan; verified by G. T. Tatevosyan and S. G. Agbalyan. A mixture of methyl ester of 5-methylfuran-2-carboxylic acid and a 20% solution of sodium hydroxide is heated for 2 hrs. The obtained 5-methylfuran-2-carboxylic acid has a m.p. of 108-109°C; yield, 83.3-87.3%. Other methods of preparation: Oxidation of 5-methylfurfural with silver oxide or alkali metal hypobromites; oxidation of 5-methyl-2-acetylfuran with potassium hypochlorite (low yield); hydrolysis of 5-methylfuran-2-cyanide. Five references, 1 Slavic (1953)

Synthesis of propylfurylcarbinol: Proposed by O. L. Mndzhoyan 44 and N. A. Babiyan; verified by G. T. Tatevosyan and N. M. Divanyan. Magnesium shavings, abs. ether and an iodine crystal are placed in a flask; an ether solution of propyl bromide is added dropwise, and the mixture is heated to boiling until the magnesium is dissolved. The mixture is cooled, and an ether solution of furfural is added. The mixture is heated for 1-1.5 hrs., and after cooling an aqueous solution of ammonium chloride is added. The obtained propylfurylcarbinol has a b.p. of 66-68°C/1.5 mm; yield, 64.1-67.9%. Two references, 1 Slavic (1956)

Card 13/25

Call Nr: AF 1135663

Syntheses of Heterocyclic Compounds (Cont.)

Page

Synthesis of 5-propoxymethylfuran-2-carboxylic acid: Proposed by V. G. Afrikyan and G. L. Papayan; verified by O. L. Mndzhoyan and O. Ye. Gasparyan. Ground sodium hydroxide is placed in alcohol (96%); and methyl ester of 5-propoxymethylfuran-2-carboxylic acid is added. The obtained 5-propoxymethylfuran-2-carboxylic acid has a m.p. of 43-44°C.; yield, 72.4-76%. One Slavic reference (1953)

46

Synthesis of phenylfurylcarbinol: Proposed by O. L. Mndzhoyan and E. R. Bagdasaryan; verified by G. T. Tatevosyan and N. M. Divanyan. Magnesium shavings, ether, and an iodine crystal are placed in a flask and an ether solution of bromobenzene is added. The mixture is heated to complete dissolution of magnesium, cooled, and an ether solution of furfural is slowly added. The mixture

48

Card 14/25

. Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

is then heated to boiling for 2.5-3.0 hrs., cooled and the reaction product decomposed with an aqueous solution of ammonium chloride. Phenylfurylcarbinol is obtained with a yield of 59.4-62.1%; b.p., 125-126°/0.5 mm. Three references, 1 Slavic (1956)

Synthesis of furan: Verified by G. T. Tatevosyan and S. P. Ekmekdzhyan. An illustration and description of an apparatus used for the synthesis are given. Furan-2-carboxylic acid is decarboxylized by heating to 200-205°C. Yield of furan, 74.7-80.2%; b.p., 31-32°/760 mm. Other methods of preparation: Furan can be obtained by removing the carbonyl group from furfural either by adding furfural to a molten mixture of KOH and NaOH or by passing its vapors over hot soda lime in the presence of catalysts (such as zinc and copper chromites and molybdates) at 300-400°C; nickel, iron, platinum, and palladium catalysts are also mentioned. A laboratory method for preparation of furan is based on decarboxylation of furan-2-carboxylic acid by

50

Card 15/25

Call Nr: AF 1135663

Syntheses of Heterocyclic Compounds (Cont.)

Page

dry distillation of the barium salt or by heating barium salt with soda lime. Furan-2-carboxylic acid can be decarboxylated by heating it in quinoline in the presence of cupric oxide. Ten references, two Slavic (1949-53)

Synthesis of furan-2-carboxylic acid and of furfuryl alcohol: Verified by V. G. Afrikyan and M. T. Grigoryan. A 30% solution of sodium hydroxide is slowly added to furfural (at 15°C). Water is then added to the mixture to dissolve the precipitated sodium salt of furan-2-carboxylic acid. Furfuryl alcohol is extracted from the solution with ether; yield 63.5-64.5%; b.p. 75-77°/15 mm. The aqueous solution containing the sodium salt of furan-2-carboxylic acid is acidified with dilute H₂SO₄ or conc. HCl, and furan-2-carboxylic acid is precipitated. Yield,

54

Card 16/25

Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

78.4-80.1%; m.p. 132-133°C. Other methods of preparation: Furan-2-carboxylic acid is obtained by oxidation of furfural with KMnO_4 and alkali metal dichromates or with atmospheric oxygen in the presence of catalysts containing silver oxide. Sodium hypochlorite was also used to oxidize furfural and 2-propionylfuran. Furan-2-carboxylic acid is obtained from furfural along with furfuryl alcohol by the reaction with sodium amide and conc. solutions of alkalies. Furfuryl alcohol may be obtained by reduction of furfural with sodium amalgam. Catalytic reduction of furfural in liquid phase under pressure at 130-160°C in the presence of copper and copper-chrome catalysts containing alkaline earth oxides is widely used. Furfuryl alcohol was obtained by reduction of furan-2-carboxylic acid with lithium aluminum hydride; yield, 85%. Furfuryl alcohol and furan-2-carboxylic acid are obtained by dismutation of furfural with sodium amide and alkalies. Thirteen references, two Slavic (1939-49)

Card 17/25

Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

Synthesis of 3-(2'-furyl)-5-mercapto-1,2,4-triazole: Proposed by A. L. Mndzhoyan and V. G. Afrikyan; verified by O. L. Mndzhoyan and N. A. Babiyan. A mixture of sodium methylate, furoyl-2-thiosemicarbazide and abs. ethyl alcohol is heated in an autoclave at 145-150°C for 3 hrs. After filtration, the residue is dissolved in water, and the solution acidified with 18-30% HCl. The product is purified by dissolution in a solution of sodium carbonate and by precipitation with 18-20% HCl. The yield of 3-(2'-furyl)-5-mercapto-1,2,4-triazole is 83.8-89.8%; m.p. 272-273°C. One Slavic reference (1953)

59

Synthesis of furoyl-2-thiosemicarbazide: Proposed by A. L. Mndzhoyan and V. G. Afrikyan; verified by N. A. Babiyan and S. S. Manucharyan. A mixture of thiosemicarbazide hydrochloride with pyridine is heated to boiling for 20-25 min., cooled to -7, -5°C, and 2-furoyl chloride is added dropwise to the mixture. The crude

60

Card 18/25

Call Nr: AF 1135663

Syntheses of Heterocyclic Compounds (Cont.)

Page

product is purified by recrystallization from glacial acetic acid. Yield, 50-55.4%; m.p. 203°C. One Slavic reference (1953).

Synthesis of furfural: Verified by G. T. Tatevosyan and N. M. Divanyan. An illustration and a description of the apparatus used for the experiments are given. A mixture of ground corn-cob, sodium chloride, and a 10% solution of H_2SO_4 is heated in the apparatus. The distilled furfural is collected in a receiver containing chloroform. Furfural is separated from the chloroform and distilled in vacuo; b.p., 70-72°/25 mm. Other methods of preparation: Treatment of xylose and other pentoses with HCl and HBr. Corn-cobs, some wood varieties, husk and chaff of oats, rice, etc. are used as raw material. Hydrolysis of the pentosans is effected by heating of the plant material with HCl or H_2SO_4 . Three references, none Slavic.

62

Card 19/25

Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

Synthesis of 5-benzyl-2-furoyl chloride: Proposed by V. G. Afrikyan and A. A. Dokhikyan; verified by G. T. Tatevosyan and N. M. Divanyan. A benzene solution of thionyl chloride is added to a benzene solution of 5-benzyl-furan-2-carboxylic acid. The mixture is heated to boiling for 4 hrs. 5-benzyl-2-furoyl chloride is obtained with a yield of 80.9-86.3%, b.p. 153-155°/mm. One Slavic reference (1953)

66

Synthesis of 5-methyl-2-furoyl chloride: Proposed by A. L. Mndzhoyan, V. G. Afrikyan and M. T. Grigoryan; verified by G. T. Tatevosyan and S. G. Agbalyan. A benzene solution of thionyl chloride is added to a benzene solution of 5-methyl-furan-2-carboxylic acid. The mixture is heated to boiling for 4-5 hrs. The obtained 5-methyl-2-furoyl chloride has a b.p. of 91-92°/35 mm; yield, 87.5-92.3%. Other methods of preparation: Reaction of

67

Card 20/25

Call Nr: AF 1135663

. Syntheses of Heterocyclic Compounds (Cont.)

Page

5-methyl-furan-2-carboxylic acid with PCl_3 or PCl_5 . Two references, none Slavic.

Synthesis of 2-furoyl chloride: Proposed by A. L. Mndzhoyan; 68 verified by V. G. Afrikyan and M. T. Grigoryan. A benzene solution of thionyl chloride is added to furan-2-carboxylic acid, and the mixture is heated to boiling for 10-12 hrs. The yield of 2-furoyl chloride is 91.1-92.0%; b.p. 89-90°/32 mm in vacuo. Other methods of preparation: 2-furoyl chloride was also obtained by heating furan-2-carboxylic acid with PCl_5 to 160°C without a solvent, but a lower yield was obtained. Chloroform was used as solvent. A patent was issued on preparation of 2-furoyl chloride by the reaction of pyromucic acid with excess of phosgene under pressure at temperatures up to 100°C. The reaction of a benzene solution of furan-2-carboxylic acid with excess of thionyl chloride is also mentioned. Five references, 1 Slavic (1976).

Card 21/25

Call Nr: AF 1135663

. Syntheses of Heterocyclic Compounds (Cont.)

Page

70

Synthesis of furfuryl chloride: Proposed by G. T. Tatevosyan and S. P. Ekmekdzhyan. Pyridine and ether are added to furfuryl alcohol. After cooling the mixture to -8° , -10°C , an ether solution of thionyl chloride is added. The temperature of the reaction mixture should not exceed $2-3^{\circ}\text{C}$. The product is extracted with ether. Furfuryl chloride is obtained with a yield of 39.4-41%; b.p. $49.1-49.4^{\circ}/26\text{ mm}$. The product cannot be stored even in sealed flasks; it must be used immediately. Other methods of preparation: The ether solution of furfuryl chloride can be prepared by the reaction of thionyl chloride with a cooled ether solution of furfuryl alcohol. The obtained solution contains about 10% furfuryl chloride. Hydrogen chloride in the presence of calcium carbide (dehydrating agent) was used instead of thionyl chloride. The amount of furfuryl in the obtained solution did not exceed 5%. The

Card 22/25

. Syntheses of Heterocyclic Compounds (Cont.)

Call Nr: AF 1135663

Page

use of chloroform as a solvent instead of ether was proposed. However, furfuryl chloride in pure state cannot be separated from solutions obtained by these methods. Three references, none Slavic.

Synthesis of β -chloroethyl ester of furan-2-carboxylic acid: 74
Proposed by A. L. Mndzhoyan and M. T. Grigoryan; verified by O. L. Mndzhoyan and E. R. Bagdasaryan. A mixture of furan-2-carboxylic acid and ethylene chlorohydrin is heated to boiling, and a rapid stream of hydrogen chloride is passed into the boiling solution for 5-6 hrs. The mixture is then cooled to room temperature and transferred to a flask containing water. The β -chloroethyl ester of furan-2-carboxylic acid is distilled in vacuo at 126-128°/10 mm; yield, 71.9-72.7%. One Slavic reference (1953).

β -Chloroethyl ester of 5-chloromethylfuran-2-carboxylic acid: Proposed by A. L. Mndzhoyan, V. G. Afrikyan, and M. T. Grigoryan; verified by O. L. Mndzhoyan and E. R. Bagdasaryan. A rapid stream of hydrogen chloride is passed into a mixture of β -chloroethyl ester of

75

Card 23/25

Call Nr: AF 1135663

Syntheses of Heterocyclic Compounds (Cont.)

Page

furan-2-carboxylic acid, paraformaldehyde, chloroform, and anhydrous zinc chloride. The reaction temperature should not exceed 24-26°C; reaction time, 2.0-2.5 hrs. The yield of the obtained product is 78.9-79.8%; b.p. 145-146°/2 mm. One Slavic reference (1953).

Synthesis of ethyl ester of furoyl-2-acetic acid: Verified by A. A. Aroyan and G. L. Papayan. Ethyl ester of furan-2-carboxylic acid is heated to 75-80°C. Sodium wire is added to it and ethyl acetate is gradually added to the mixture. After the dissolution of sodium, the mixture is heated to 90-95°C, and sodium wire and ethyl acetate are again added. The mixture is solidified in about 20-30 min., after which it is dissolved in benzene. The addition of sodium wire and ethyl acetate followed by the addition of benzene (as above) is repeated six times. Reaction time, 10-12 hrs. The mixture is heated on a water

77

Card 24/25

Call Nr: AF 1135663

Syntheses of Heterocyclic Compounds (Cont.)

Page

bath for 8-12 hrs. at 90-95°C. The content of the flask is cooled and decomposed with ice water. Then the reaction mixture is added to dilute HCl, the benzene layer is separated, and the water layer is extracted with ether (three times). The ether solutions are added to the benzene solution, dried, the solvent removed, and the residue distilled in vacuo. The 119-125°/2 mm fraction is redistilled. The product obtained has a b.p. of 123-124°/2 mm; yield, 77.6-83.8%. Other methods of preparation: The ethyl ester of furoyl-2-acetic acid may be obtained by condensation of ethyl acetate with methyl ester of furan-2-carboxylic acid in the presence of sodium methylate; yield, 68.2%. Ethyl furoyl-2-acetate may be obtained by heating ethyl tert-butyl furoyl malonate with p-toluenesulfonic acid; yield 70%. Four references, none Slavic.

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